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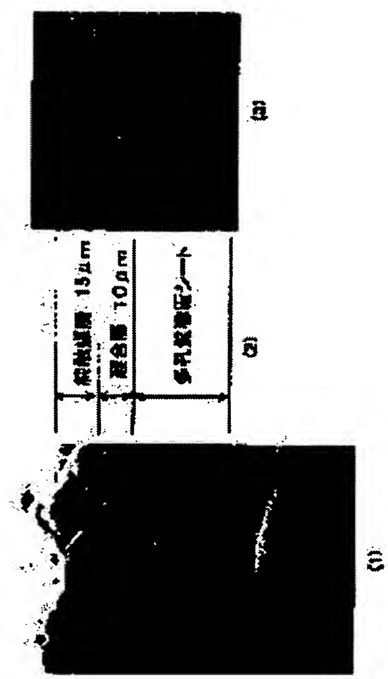
(54) ELECTRODE, MEMBRANE-ELECTRODE COMPLEX AND ITS PRODUCTION AS WELL AS FUEL CELL USING THESE

(57)Abstract:

PROBLEM TO BE SOLVED: To provide an electrode having a less mixture layer formed with an electrode catalyst layer infiltrated into an electrode substrate when using a porous conductive sheet as the electrode substrate.

SOLUTION: The electrode comprises, at least, an electrode substrate and an electrode catalyst layer, the electrode catalyst layer being infiltrated into the electrode substrate to form the mixture layer, the mixture layer having a thickness of 20 μm or less.



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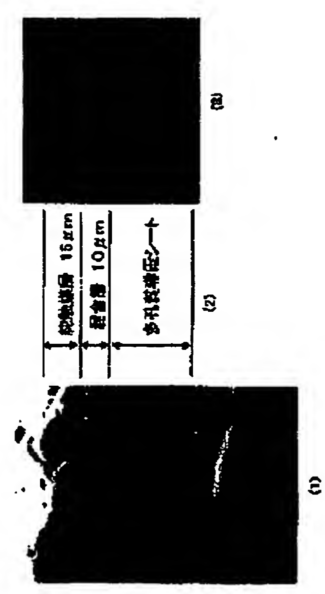
(54)【発明の名称】　電極、膜－電極複合体およびその製造方法並びにこれらを用いた燃料電池

(57)【要約】
【課題】　多孔質導電シートを電極基材とする際の、電極基材への電極触媒層の浸み込んだ混合層の少ない電極を提供すること。
【解決手段】　少なくとも、電極基材と電極触媒層とから構成される電極において、該電極基材の中に該電極触媒層が浸み込んで混合層を形成しているとともに、該混合層の厚さが２０μm以下であることを特徴とする電極



【特許請求の範囲】

【請求項１】少なくとも、電極基材と電極触媒層とから構成される電極において、該電極基材の中に該電極触媒層が浸み込んで混合層を形成しているとともに、該混合層の厚さが２０μm以下であることを特徴とする電極。

【請求項２】混合層の厚さが１０μm以下である請求項１記載の電極。

【請求項３】電極基材が多孔質導電シートである請求項１または２に記載の電極。

【請求項４】多孔質導電シートが無機導電性繊維を用いた織布構造あるいは不織布構造のものである請求項３に記載の電極。

【請求項５】無機導電性繊維が炭素繊維である請求項４に記載の電極。

【請求項６】電極基材が導電性粒子を含む請求項１～５のいずれかに記載の電極。

【請求項７】導電性粒子が炭素材である請求項６に記載の電極。

【請求項８】電極基材がフッ素原子を含有するポリマを含む請求項１～７のいずれかに記載の電極。

【請求項９】電極触媒層が、少なくとも、白金、パラジウム、金、ルテニウム、及びイリジウムからなる群から選ばれる一種以上の元素を含む請求項１～８のいずれかに記載の電極。

【請求項１０】電極触媒層がカーボンブラックを含む請求項１～９のいずれかに記載の電極。

【請求項１１】電極触媒層がフッ素原子を含有するポリマを含む請求項１～１０のいずれかに記載の電極。

【請求項１２】電極触媒層がプロトン交換基を有するポリマを含む請求項１～１１のいずれかに記載の電極。

【請求項１３】電極触媒塗液を電極基材上に塗布することを特徴とする請求項１～１２のいずれかに記載の電極の製造方法。

【請求項１４】電極基材と電極触媒塗液との静的接触角が５０°以上である請求項１３に記載の電極の製造方法。

【請求項１５】請求項１～１２のいずれかに記載の電極と、プロトン交換膜とから構成される膜－電極複合体。

【請求項１６】プロトン交換膜がフッ素原子含有ポリマである請求項１５記載の膜－電極複合体。

【請求項１７】フッ素原子含有ポリマがスルホン酸基を有するフルオロアルキルエーテル側鎖とフルオロアルキル主鎖からなるポリマである請求項１６に記載の膜－電極複合体。

【請求項１８】請求項１～１２のいずれかに記載の電極２枚の間にプロトン交換膜を前記各電極の電極触媒層側が該プロトン交換膜に対面するように配置し、前記２枚の電極で該プロトン交換膜を挟持させて接合することを特徴とする膜－電極複合体の製造方法。

【請求項１９】プロトン交換膜の表裏両面に電極触媒層を設ける工程（工程Ａ）、該電極触媒層の両外側面に電極基材を設ける工程（工程Ｂ）をこの順で行うことを特徴とする膜－電極複合体の製造方法。

【請求項２０】工程Ａが電極触媒塗液をプロトン交換膜上に塗布する工程を含むものである請求項１９に記載の膜－電極複合体の製造方法。

【請求項２１】工程Ａが電極触媒塗液を転写基材上に塗布して電極触媒層を形成し、これをプロトン交換膜上に転写するものである請求項１９に記載の膜－電極複合体の製造方法。

【請求項２２】工程Ｂが電極基材を構成する物質を塗工するものである請求項１９～２１のいずれかに記載の膜－電極複合体の製造方法。

【請求項２３】電極基材を構成する物質が炭素短繊維とフッ素原子含有ポリマを含む分散液である請求項２２に記載の膜－電極複合体の製造方法。

【請求項２４】請求項１～１２のいずれかに記載の電極を用いた電気化学装置。

【請求項２５】請求項１５～１７のいずれかに記載の膜－電極複合体を用いた電気化学装置。

【請求項２６】請求項１～１２のいずれかに記載の電極を用いた水電解装置。

【請求項２７】請求項１５～１７のいずれかに記載の膜－電極複合体を用いた水電解装置。

【請求項２８】請求項１～１２のいずれかに記載の電極を用いた燃料電池。

【請求項２９】請求項１５～１７のいずれかに記載の膜－電極複合体を用いた燃料電池。

【請求項３０】固体高分子型電解質を用いる請求項２８または２９に記載の燃料電池。

【請求項３１】請求項２８～３０のいずれかに記載の燃料電池を電力供給源とする移動体。

【請求項３２】請求項２８～３０のいずれかに記載の燃料電池を電力供給源とする自動車。

【発明の詳細な説明】

【０００１】

【発明の属する技術分野】本発明は、燃料電池あるいは種々の電気化学装置に用いられる電極あるいは膜－電極複合体とそれらの製造方法に関するものである。

【０００２】

【従来の技術】燃料電池は、低排出物、高エネルギー効率で環境への負担の低い発電装置である。このため、近年の地球環境保護への高まりの中で再び脚光を浴びている。従来の大規模発電施設に比べ比較的小規模の分散型発電施設、自動車や船舶など移動体の発電装置として、将来的にも期待されている発電装置である。

【０００３】燃料電池には、用いられる電解質の種類により、固体高分子型、リン酸型、固体酸化物型、溶融炭酸塩型、アルカリ型などの種類がある。なかでも固体高分子型燃料電池は、他の燃料電池に比べて、運転温度が

低温で起動時間が短く、高出力が得やすい、小型軽量化が見込める、振動に強いなどの特徴を有し移動体の電力供給源に適している。

【０００４】燃料電池は、発電を担う反応の起こるアノードとカソードの電極と、アノードとカソード間のイオン伝導体となる電解質とがそれぞれの間でセパレータで挟まれたセルをユニットとして構成されている。電極は、ガス拡散の促進と集（給）電を行う電極基材（集電体とも云う）と、実際に電気化学反応場となる電極触媒層とから構成されている。たとえば固体高分子型燃料電池のアノード電極では、燃料ガスが触媒表面で反応してプロトンと電子を生じ、電子は電極基材に伝導し、プロトンは電解質のプロトン交換膜へと伝導する。このため、アノード電極には、ガス拡散性、電子電導性、イオン電導性が良好なことが要求される。一方、カソード電極では、酸化ガスが触媒層表面で、電解質から伝導してきたプロトンと、電極基材から伝導してきた電子とが反応して水を生成する。このため、ガス拡散性、電子電導性、イオン電導性とともに、生成した水を効率よく排出することも必要となる。

【０００５】このような点から、電極基材（集電体）には導電性を有しガス透過性の良好な多孔質導電シートが用いられてきた。たとえば、特開平６－２０７１０号公報、特開平７－３２６３６２号公報、あるいは、特開平７－２２０７３５号公報のものが提案されている。これらに開示された集電体は、短い長さの炭素繊維が炭素で結着されてなる多孔質炭素板からなる。

【０００６】

【発明が解決しようとする課題】上記の多孔質導電シートはガス透過性は良好であるが、そのシート上に電極触媒層を塗工すると空孔内への触媒塗液の浸み込み現象が見られた。この触媒浸み込み現象により、有効に利用されない触媒が増すこととなる。燃料電池においては貴金属の触媒が用いられるために、有効に使われない触媒が増すことは電極のコストアップに繋がるものである。特に、固体高分子型燃料電池は自動車用途への期待が高い。自動車用途への適応には、性能と共にコストも重要な因子となる。現在の固体高分子型燃料電池は、低コスト化がなされればより一層の普及が見込まれている。このため、触媒浸み込みの少ない電極が求められていた。

【０００７】本発明は、上記課題を解決し、触媒浸み込みの少ない電極が得られることにより、触媒の利用効率が向上し、触媒量低減による低コスト化電極が得られることを目的とする。

【課題を解決するための手段】本発明において、上記課題を解決するため下記構成を有する。

【０００８】すなわち、本発明の電極は、少なくとも電極基材と電極触媒層とから構成される電極において、該電極基材の中に該電極触媒層が浸み込んで混合層を形成しているとともに、該混合層の厚さが２０μm以下であることを特徴とする。

【０００９】また、本発明の電極の製造方法は、電極基材上に電極触媒層を設けることにより製造されるものであるが、電極触媒塗液を該電極基材上に塗布して該電極触媒層を設けることを特徴とする。

【００１０】さらに、本発明の電極は、膜-電極複合体（ＭＥＡ）に適用されるほか、通常の電気化学装置、特に固体高分子型燃料電池にも適用され、この燃料電池を用いた移動体や自動車にも適用されるものである。

【００１１】

【発明の実施の形態】以下、本発明の好ましい実施の形態を説明する。

【００１２】本発明は、少なくとも電極基材と電極触媒層とから構成される電極において、該電極基材の中に該電極触媒層が浸み込んでいる混合層の厚さが２０μm以下であることを特徴とするものであり、ここで用いられる電極基材や電極触媒層はとくに限定されるものではない。

【００１３】本発明における混合層とは電極基材の中に電極触媒層が浸み込んでいる層であるので、電極基材を含まない電極触媒層の構成成分（例えば、触媒金属、触媒粒子、カーボンブラック、フッ素原子を含有するポリマ等）のみにより構成される層（以下、純電極触媒層という）は、前記混合層には含まれない。従って、純電極触媒層の厚さは、本発明の混合層の厚さに算入されることはなく、除外して計算される。但し、本発明の電極において、前記純電極触媒層も有することを妨げるものではない。よって、本発明の電極触媒層には、混合層とともに純電極触媒層も含まれることがある。

【００１４】本発明において、電極基材の中に電極触媒層が浸み込んでいるとは、電極基材の少なくと一部の層乃至は領域において、電極基材の構成材が存在しない空隙部分に電極触媒の構成材が存在している状態を意味する。確かに、既に形成されている電極基材に対して固体化乃至は固定化されていない液体状態の電極触媒構成材料が浸み込んで形成されるという製造方法は、本発明の混合層乃至は電極触媒層の好適な製造法の１つではある。しかし、本発明の混合層乃至は電極触媒層は、必ずしもこの製造方法で形成されたものであると限定していることを意味するものではない。

【００１５】本発明における混合層の厚さとは、平均厚さであり、従って、局所的に本発明の数値範囲を満たさない箇所があっても、平均値で満たしている限り、本発明の技術範囲内であることは言うまでもない。前記混合層の厚さは、好ましくは１５μm以下、さらに好ましくは、１０μm以下である。尚、特に限定されるものではないが、３μm以上であることが好ましく、５μm以上であることがより好ましい。前記上限値を上回ると浸み込みが多く有効に用いられる触媒量が低下することとなり、前記下限値を下回ると膜-電極複合体を作成したと

きに抵抗が大きくなることがあり好ましくないからである。

【００１６】本発明において、電極基材中に電極触媒層が浸み込んでいる混合層の厚さは、電極断面の走査型電子顕微鏡（ＳＥＭ）観察によって確認できる。一般的には、電極基材は多孔質構造であり、電極触媒層は粒子を充填した構造であるため、多孔質の電極基材中への電極触媒粒子の浸み込んだ混合層が観察される。また、電極基材が炭素粉末などの導電性微粒子を含む場合のように、電極基材に電極触媒層が浸み込んでいる混合層がはっきり観察できない場合がある。このような場合には、ＳＥＭとＸ線マイクロアナリシス（ＸＭＡ）を併用（ＳＥＭ－ＸＭＡ）することで、電極触媒に含まれる白金などの貴金属触媒が電極基材のどこまで浸み込んでいるかを観察することにより混合層の厚さを求めることが可能である。上記のＳＥＭあるいはＳＥＭ－ＸＭＡ以外にも、特に限定されることなくさまざまな手法で混合層の厚みを求めることは可能である。

【００１７】ＳＥＭ－ＸＭＡにおいては、以下の手順で純電極触媒層と混合層を測定する。まず、ＳＥＭ観察から導電性シートと純電極触媒層の界面を確認し、純電極触媒層の厚さを測定する。次に、ＸＭＡ測定により電極触媒に用いられるＰｔの存在を画面の濃淡で確認し、純電極触媒層と導電性シートに浸み込んだ混合層の合計の厚さを測定する。両者の差から混合層の厚みを求めることが可能となる。

【００１８】本発明に用いられる電極基材としては、電気抵抗が低く、集（給）電を行えるものであればとくに限定されることなく用いることが可能であるが、特に多孔質導電シートにおいて本発明の特徴が発現されるものである。電極基材の構成材としては、たとえば、導電性無機物質を主とするものが挙げられ、この導電性無機物質としては、ポリアクリロニトリルからの焼成体、ピッチからの焼成体、黒鉛及び膨張黒鉛などの炭素材、ステンレススチール、モリブデン、チタンなどが例示される。導電性無機物質の形態は繊維状あるいは粒子状など特に限定されないが、燃料電池などのように電極活物質に気体を用いる電気化学装置に用いる場合、ガス透過性の点から繊維状導電性無機物質（無機導電性繊維）特に炭素繊維が好ましい。無機導電性繊維を用いた多孔質導電シートとしては、織布あるいは不織布いずれの構造も使用可能である。たとえば、東レ（株）製カーボンペーパーＴＧＰシリーズ、ＳＯシリーズ、Ｅ－ＴＥＫ社製カーボンクロスなどが用いられる。

【００１９】本発明に用いられる電極基材としては、厚み方向に２．９ＭＰａの一様な面圧を加えたときの厚みが０．０２～０．３ｍｍであるものが好ましい。より好ましくは０．０４～０．２ｍｍである。０．０２ｍｍより薄い場合、燃料電池に用いる際にセパレータのガス流路に電極基材が埋没し、面方向への拡散・透過性が低くなり、強度が弱く作業性に乏しくなる。０．３ｍｍよりも厚い場合、厚み方向の電気抵抗が増えてくる。なお、厚みは、電極基材を均一な厚みで平滑な表面を有する２枚のガラス状炭素板で挟み、２．９ＭＰａの一様の面圧で加圧し、電極基材を挟まないときと挟んだときとの上下の圧子の間隔の差から求める。圧子の間隔の測定においては、圧子の中心点を挟む両端で微小変位検出装置により圧子の間隔を測定し、両端の間隔の平均値として圧子の間隔を算出する。一様な面圧とするために、一方の圧子は球座で受けて上下の圧子の加圧面のなす角度を可変にする。

【００２０】厚み方向に２．９ＭＰａの一様な面圧を加えたとき上記の厚みとなる電極基材の、１３ｋＰａの面圧で測定した厚みは０．１～２．０ｍｍが好ましく、０．２～１．２ｍｍがより好ましい。２ｍｍを超えると電極基材が嵩高になり、電極基材が厚み方向へ向いたり、電極基材の強度が弱くなる。０．１ｍｍ未満の厚みにするためには、多量の高分子物質によって電極基材の結着を強固に行う必要がでてくる。

【００２１】電極基材の目付としては１０～２２０ｇ／ｍ^{2}であるのが好ましい。より好ましくは２０～１２０ｇ／ｍ^{2}である。１０ｇ／ｍ^{2}未満では電極基材の強度が低くなる。また、高分子電解質膜、触媒層、電極基材の一体化時や電池に組んだときに電極基材が薄くなり面方向への拡散・透過効果が不十分になる。２２０ｇ／ｍ^{2}を超えると電池に組んだ時に電極基材が厚くなり抵抗が大きくなる。

【００２２】電極基材の密度は、厚み方向に２．９ＭＰａの一様な面圧を加えたときに０．３～０．８ｇ／ｃｍ^{3}であるのが好ましい。より好ましいのは０．３５～０．７ｇ／ｃｍ^{3}であり、さらに好ましいのは０．４～０．６ｇ／ｃｍ^{3}である。厚み方向に２．９ＭＰａの一様な面圧を加えたときの電極基材の密度は、電極基材の目付と厚み方向に２．９ＭＰａの一様な面圧を加えたときの電極基材の厚みから計算によって求める。電極基材は、拡散・透過性を高くするためには気孔率を高くする必要があるが、厚み方向に２．９ＭＰａの一様な面圧を加えたときの密度が０．８ｇ／ｃｍ^{3}よりも大きくなると気孔率が下がり、拡散・透過性が不十分になる。また、０．３ｇ／ｃｍ^{3}よりも小さいと、厚み方向の抵抗値が大きくなる。

【００２３】電極基材は、厚み方向への面圧による加圧を行わない状態で、厚み方向に１４ｃｍ／秒の空気を透過させたときの圧力損失が、９８Ｐａ（１０ｍｍＡｑ）以下であるのが電極基材のガス拡散性の点で好ましい。より好ましいのは２９Ｐａ（３ｍｍＡｑ）以下であり、さらに好ましいのは９．８Ｐａ（１ｍｍＡｑ）以下である。

【００２４】電極基材の引っ張り強さは、０．４９Ｎ／１０ｍｍ幅以上が好ましく、１．９６Ｎ／１０ｍｍ幅以

上がより好ましく、４．９Ｎ／１０ｍｍ幅以上が更に好ましい。引っ張り強さが低いと、電極機材の高次加工において、シートが破損する可能性が増すという問題がある。

【００２５】電極基材は、高分子電解質膜、触媒層、電極基材の一体化時や電池として使用する際に厚み方向に加圧されて壊れることがある。また、電池として使用するときには溝付セパレータと向かい合った状態で厚み方向に加圧されるため、溝付セパレータの山と向かい合う部分に大きな圧力がかかるのに加えて、山と谷の境と向かい合う部分が壊れやすい。電極基材が壊れると、壊れた無機導電性物質の脱落、電極基材の強度低下、面方向の電気抵抗増大等が起こり、電極性能が低下することがある。

【００２６】上記のことから、電極基材は、厚み方向に２．９ＭＰａの一様な面圧を２分間加え、その面圧を解除した後の重量減少率が３％以下であるのが好ましい。重量減少率が３％より高い電極基材は面圧解除後弱くなっており、ハンドリングで壊れやすいという問題があるからである。これにより、加圧時に壊れにくく、電極基材の破壊により燃料電池が使用できなくなるのを防止できる。好ましくは２％以下、さらに好ましくは１％以下である。

【００２７】なお、重量減少率の測定は、以下のようにして行う。まず、電極基材を直径４６ｍｍの円形にカットし、重量を測定する。次に、その電極基材よりも大きく、平滑表面を有する２枚のガラス状炭素板でカットした電極基材を挟み、電極基材の面積当たり２．９ＭＰａの圧力になるよう加圧し、２分保つ。圧力を取り除いて電極基材を取り出し、その面方向を垂直方向に向けて３０ｍｍの高さから落下させる。この落下を１０回行った後に重量を測定し、重量減少率を算出する。

【００２８】電極基材の電気抵抗Ｒの測定は、次による。幅５０ｍｍ、長さ２００ｍｍ、厚み１．５ｍｍの表面が平滑な平面を有するガラス状炭素板の片面に、幅５０ｍｍ、長さ２００ｍｍ、厚み０．１ｍｍの銅箔が貼着された試験電極板が、２枚用意される。２枚の試験電極板は、実質的に均一な間隔を保ち、ガラス状炭素板の面同士が対向して位置せしめられる。２枚の試験電極板のそれぞれの一端には、電流用の端子が、それぞれの他端には、電圧用の端子が、設けられている。直径４６ｍｍの円形に切り出されたシートが、前記間隙に挿入され、２枚の試験電極板の中央部に、載置される。載置されたシートに０．９８ＭＰａの圧力が作用するように、試験電極板が移動される。電流用の端子にて、２枚の試験電極板間に１Ａの電流が流される。電圧用の端子にて、この時の電圧Ｖ（Ｖ）が測定される。測定された電圧Ｖの値が用いられ、次式により、抵抗Ｒ（ｍΩ・ｃｍ^2）が求められる。

Ｒ＝Ｖ×２．３×２．３×π×１０００

ここで、πは円周率である。

【００２９】多孔質導電性シートの電気抵抗は、１００ｍΩ・ｃｍ^{2}以下であることが好ましく、５０ｍΩ・ｃｍ^{2}以下であることがより好ましく、１５ｍΩ・ｃｍ^{2}以下であることが更に好ましい。後述のように撥水性のフッ素樹脂を含む電極基材の電気抵抗は、１５０ｍΩ・ｃｍ^{2}以下であることが好ましく、７０ｍΩ・ｃｍ^{2}以下であることがより好ましく、３０ｍΩ・ｃｍ^{2}以下であることが更に好ましい。

【００３０】電極基材には、上記の電極基材に加えて、実質的に二次元平面内において無作為な方向に配向された無機導電性繊維を高分子物質で結着してなる紙状シートを含み、無機導電性繊維の長さが、少なくとも３ｍｍで、かつ、シートの厚みの少なくとも５倍である多孔質導電シートを用いることもできる。ここで、シートの厚みはＪＩＳ　Ｐ８１１８に準じて測定する。測定時の面圧は１３ｋＰａとする。無機導電性繊維が実質的に二次元平面内において配向されているということの意味は、無機導電性繊維がおおむね一つの面を形成するように横たわっているという意味である。このことにより無機導電性繊維による対極との短絡や無機導電性繊維の折損を防止することができる。

【００３１】電極基材の強度やハンドリング性を高くし、無機導電性繊維を実質的に二次元平面内において配向させるために、無機導電性繊維の長さは少なくとも３ｍｍ以上であるが、好ましくは４．５ｍｍ以上、さらに好ましくは６ｍｍ以上とする。３ｍｍ未満では、強度、ハンドリング性を保つのが難しくなる。また、無機導電性繊維を実質的に二次元平面内において無作為な方向に配向させるために、無機導電性繊維の長さは電極基材の厚みの５倍以上、好ましくは８倍以上、さらに好ましくは１２倍以上とする。５倍未満では、二次元への配向の確保が難しくなる。無機導電性繊維の長さの上限は、実質的に二次元平面内において無作為な方向に配向させるためには３０ｍｍ以下が好ましく、１５ｍｍ以下がより好ましく、８ｍｍ以下がさらに好ましい。無機導電性繊維が長すぎると分散不良を発生しやすく、多数の繊維が束状のまま残る場合がある。その場合、束状の部分は空隙率が低く、加圧時の厚みが厚くなるために加圧時に高い圧力がかかり、電極基材の破壊や、高分子電解質膜や電極触媒層の局部的な薄層化等の問題が起こりやすくなる。

【００３２】また、無機導電性繊維の形態は、繊維による対極との短絡をより完全に防止できるように、直線状であるのが好ましい。ここで、直線状の無機導電性繊維とは、無機導電性繊維を曲げる外力を取り除いた状態で繊維の長さ方向にある長さＬ（ｍｍ）をとったときに、長さＬに対する直線性からのずれΔ（ｍｍ）を測定し、Δ／Ｌがおおむね０．１以下であるものをいう。一方、非直線状の繊維は、実質的に二次元平面内において無作

為な方向に配向させるときに三次元方向を向きやすいという欠点がある。

【００３３】電極基材の作成において、無機導電性繊維を実質的に二次元平面内において無作為な方向に配向させる方法としては、液体の媒体中に無機導電性繊維を分散させて抄造する湿式法や、空気中で無機導電性繊維を分散させて降り積もらせる乾式法がある。無機導電性繊維を確実に実質的に二次元平面内において配向させるため、また、無機導電性繊維の強度を高くするためには、湿式法、特にいわゆる抄紙法が好ましい。

【００３４】電極基材において、加圧時の無機導電性物質の折損を防止し、前述のように電極基材の重量減少率を３％以下とするために、使用する繊維は、炭素繊維をカットした炭素短繊維が好ましく、熱処理時に張力をかけたものがより好ましく、熱処理時に延伸したものがさらに好ましい。

【００３５】炭素繊維としては、ポリアクリロニトリル（ＰＡＮ）系炭素繊維、フェノール系炭素繊維、ピッチ系炭素繊維、レーヨン系炭素繊維などが例示される。なかでも、ＰＡＮ系炭素繊維が好ましい。ＰＡＮ系炭素繊維はピッチ系炭素繊維にくらべて圧縮強さ、引張破断伸度が大きく、折れにくい。このことは、炭素繊維を構成する炭素の結晶化の相異によると考えられる。折れにくい炭素繊維を得るためには、炭素繊維の熱処理温度は２，５００℃以下が好ましく、２，０００℃以下がより好ましい。

【００３６】本発明の電極基材中に用いられる炭素短繊維は、直径Ｄ（μｍ）と、引張強さσ（ＭＰａ）と、引張弾性率Ｅ（ＭＰａ）との関係が次式を満足しているのがよい。そのような炭素短繊維からなる電極基材は、壊れにくいためである。すなわち、炭素短繊維の直径が細く、引張強さが強く、引張弾性率が低いほうが炭素短繊維は折れにくく、加圧時に電極基材が壊れにくくなる。

$\sigma/(E\times D)\geq 0.5\times 10^{-3}$

ここで、炭素繊維の引張強さ、引張弾性率はＪＩＳ Ｒ７６０１に準じて測定する。偏平な断面の炭素繊維の場合、長径（ａ）と短径（ｂ）の平均値（（ａ＋ｂ）／２）を直径とする。種類の異なる炭素短繊維が混合されている場合、Ｄ、σ、Ｅについてそれぞれ重量平均した値を用いる。好ましくは$\sigma/(E\times D)\geq 1.1\times 10^{-3}$であり、より好ましくは$\sigma/(E\times D)\geq 2.4\times 10^{-3}$である。

【００３７】炭素短繊維の引張破断伸度は、電極基材の強度のため、０．７％以上であるのが好ましく、より好ましくは１．２％以上であり、さらに好ましくは１．８％以上である。引張破断伸度は引張強さ（σ）を引張弾性率（Ｅ）で除した値である。

【００３８】また、炭素短繊維の折損は様々な状況で発生するため、炭素短繊維の引張強さは５００ＭＰａ以上であるのが好ましく、１，０００ＭＰａ以上であるのがより好ましく、２，０００ＭＰａ以上であるのがさらに好ましい。

【００３９】電極基材に用いられる無機導電性繊維の直径は、２０μｍ以下であるのが好ましい。より好ましいのは１２μｍ以下、さらに好ましいのは８μｍ以下である。電極基材の表面には、無機導電性繊維の直径の５～１０倍の直径の空隙が観察される。この空隙は繊維径が太くなると大きくなる。本発明の導電性中間層は、電極触媒層がこの空隙に浸み込むことにより電極性能が低下することを抑制するものである。この空隙が大きすぎると導電性中間層を厚くする必要が生じ、ガス透過性や水の排出性を阻害するので、繊維径は細い方が好ましい。また、無機導電性繊維は細いほど厚み方向の加圧時に折れにくい。一方、無機導電性繊維の直径が細くなりすぎると、一体化時に触媒層の電極基材への浸入が起こりにくくなるため、繊維径は２μｍ以上であるのが好ましい。直径の異なる繊維が混合されている場合は、重量平均によって直径を求める。

【００４０】電極基材に用いられる無機導電性繊維の体積抵抗率は、電極基材の低抵抗化のため２００μΩ・ｍ以下が好ましく、５０μΩ・ｍ以下がより好ましく、１５μΩ・ｍ以下がさらに好ましい。無機導電性繊維の体積抵抗率の測定はＪＩＳ Ｒ７６０１に準じて行う。前記測定処方で定められた繊維長さが得られない場合、得られた繊維長さで測定を行う。

【００４１】電極基材に炭素繊維を用いる場合、Ｘ線光電子分光分析法による表面の酸素原子と炭素原子との原子数比（酸素原子数／炭素原子数）が０．３５以下、好ましくは０．２０以下、さらに好ましくは０．１０以下であるものがよい。湿式抄紙法によって電極基材を得る場合、酸素原子と炭素原子との原子数比が高いと炭素短繊維の分散が難しくなって分散不良が増加するためである。０．３５を超えると均一な電極基材を得ることが難しくなる。酸素原子と炭素原子との原子数比を低くするためには、炭素繊維の表面処理やサイジング剤の付与をやめたり、不活性または還元雰囲気中での熱処理によって表面の酸素原子を取り除く方法がある。

【００４２】電極基材は、水の滞留によるガス拡散・透過性の低下を防ぐために行う撥水処理、水の排出路を形成するための部分的撥水、親水処理や、抵抗を下げるために行われる炭素質粉末の添加等を行うことも好ましい実施態様である。

【００４３】本発明の電極基材は、上述のように導電性無機繊維からなる多孔質導電シートを用いる場合、圧縮時の厚み低下抑制、密度の向上、電気抵抗の低減などの点から、導電性粒子、特に導電性無機粒子を含むことも好ましい実施態様である。このような導電性無機粒子としては、電気抵抗や耐食性の点から炭素材、特に炭素粒子が好ましい。

【００４４】特に、柔軟性を有する導電性無機粒子がシ

ート状に配列されてなる多孔質導電シートを電極基材に用いることも好ましい。これにより構成成分の脱落が少ない、あるいは、機械的力が作用しても壊れ難く、電気抵抗が低く、かつ、安価な電極基材を提供するという目的が可能となる。特に、柔軟性を有する導電性無機粒子として、膨張黒鉛粒子を用いることで上記目的が達成可能である。

【００４５】ここで、膨張黒鉛粒子とは、黒鉛粒子が、硫酸、硝酸などにより層間化合物化された後、急速に加熱することにより膨張せしめられて得られる黒鉛粒子をいう。通常、膨張黒鉛粒子の結晶構造における層間距離は、原料黒鉛粒子のそれの約５０～５００倍である。

【００４６】膨張黒鉛粒子は、それ自体、形状の変形性に富む。この性質は、柔軟性と云う言葉で表現される。この柔軟性は、膨張黒鉛粒子とそれに隣接する他の物体に対する膨張黒鉛粒子の形態的融和性により観察される。この形態的融和性は、膨張黒鉛粒子同士が、少なくとも一部が重なり合った状態で加圧作用を受けると、加圧状態に応じて、互いに変形し、粒子同士が少なくとも部分的に接合することにより観察される。また、この形態的融和性は、膨張黒鉛粒子と、気体透過性が確保される状態でそれらがシート状に配列せしめられる場合に用いられる補助材（例えば、カーボンブラックなどの従来用いられている柔軟性を有しない導電性無機粒子、あるいは、炭素繊維などの従来用いられている無機導電性繊維）とが、共に加圧された場合、膨張黒鉛粒子が、補助材の外形状に沿って、変形され、この補助材に接合されることにより観察される。

【００４７】本発明の電極基材は、柔軟性を有する導電性微粒子に加えて、他の導電性粒子や導電性繊維を含むことも好ましい実施態様であるが、この導電性繊維と導電性粒子の双方が、無機材料からなることにより、耐熱性、耐酸化性、耐溶出性に優れた電極基材が得られる。柔軟性を有しない導電性無機粒子としては、例えば、カーボンブラック粉末、黒鉛粉末、金属粉末、セラミックス粉末などを含んでも良いが、電子電導性と耐触性の点から、カーボンブラック、黒鉛質や炭素質の炭素材が好ましく挙げられる。このような炭素材としては、オイルファーネスブラック、チャネルブラック、ランプブラック、サーマルブラック、アセチレンブラックなどのカーボンブラックが、電子電導性と比表面積の大きさから好ましいものである。オイルファーネスブラックとしては、キャボット社製バルカンＸＣ－７２、バルカンＰ、ブラックパールズ８８０、ブラックパールズ１１００、ブラックパールズ１３００、ブラックパールズ２０００、リーガル４００、ライオン社製ケッチェンブラックＥＣ、三菱化学社製＃３１５０、＃３２５０などが挙げられ、アセチレンブラックとしては電気化学工業社製デンカブラックなどが挙げられる。またカーボンブラックのほか、天然の黒鉛、ピッチ、コークス、ポリアクリロニトリル、フェノール樹脂、フラン樹脂などの有機化合物から得られる人工黒鉛や炭素などがある。また、これら炭素材を後処理加工した炭素材も用いることが可能である。このような炭素材の中でも、特に、キャボット社製のバルカンＸＣ－７２、電気化学工業社製のデンカブラック、ライオン社製のケッチェンブラックなどが電子電導性の点から好ましく用いられる。

【００４８】なお、電極基材に対する導電性粒子の添加量としては、要求される電極特性や用いられる物質の比表面積や電子抵抗などに応じて適宜決められるべきものであるが、電極基材中の重量比率として１～８０％が好ましく、２０～６０％がさらに好ましい。電子伝導体は、少ない場合は電子抵抗が低くなり、多い場合はガス透過性を阻害するなど、いずれも電極性能を低下させる。

【００４９】本発明の電極基材は、上記の導電性粒子のほか、高分子物質を添加することも可能である。これにより圧縮や引張りに強くなり、強度、ハンドリング性を高め、無機導電性物質が電極基材から外れたり、電極基材の厚み方向を向くのを防止できる。特に、無機導電性短繊維を抄紙して多孔質導電シートからなる電極基材を作成する際には、高分子物質を結着剤として用いることは必須である。高分子物質を結着させる方法としては、無機導電性物質を実質的に二次元平面内において無作為な方向に配向させるときに繊維状、粒状、液状の高分子物質を混合する方法と、無機導電性物質が実質的に二次元平面内において無作為な方向に配向された集合体に繊維状、液状の高分子物質を付着させる方法等がある。液状の概念には、エマルジョン、ディスパージョンやラテックス等、液体中に高分子物質の微粒子が分散して実質的に液体として取り扱うことができるものも含まれる。無機導電性物質の結着を強くしたり、電極基材の電気抵抗を低くしたりするためには、無機導電性物質を結着する高分子物質は繊維状、エマルジョン、ディスパージョン、ラテックスであるのが好ましい。繊維状の高分子物質の場合、含有率を低くするため、フィラメント糸を使用することが好ましい。

【００５０】無機導電性物質を結着する高分子物質としては、炭素またはケイ素を主鎖に持つ高分子物質が好ましく、たとえば、ポリビニルアルコール（ＰＶＡ）、ポリ酢酸ビニル（酢ビ）、ポリエチレンテレフタレート（ＰＥＴ）、ポリプロピレン（ＰＰ）、ポリエチレン、ポリスチレン、ポリ塩化ビニル、ポリ塩化ビニリデン、アクリル樹脂、ポリウレタン等の熱可塑性樹脂や、フェノール樹脂、エポキシ樹脂、メラミン樹脂、尿素樹脂、アルキド樹脂、不飽和ポリエステル樹脂、アクリル樹脂、ポリウレタン樹脂等の熱硬化性樹脂のほか、熱可塑性エラストマー、ブタジエン・スチレン共重合体（ＳＢＲ）、ブタジエン・アクリロニトリル共重合体（ＮＢＲ）等のエラストマー、ゴム、セルロース、パルプ等を

用いることができる。フッ素樹脂等の撥水性の樹脂を用い、無機導電性物質の結着と同時に電極基材の撥水化処理を行ってもよい。

【００５１】電極基材を加圧時に壊れにくくするためには、無機導電性物質を結着する高分子物質は軟らかいほうがよく、高分子物質を繊維状または粒状の形態で用いる場合には、高分子物質は、熱可塑性樹脂、エラストマー、ゴム、セルロース、パルプなどの柔らかい高分子物質を用いると電極基材が加圧時に壊れることが少なくなるので好ましい。また、高分子物質を液状の形態で用いる場合には、高分子物質は、熱可塑性樹脂、エラストマー、ゴムや、熱可塑性樹脂、エラストマー、ゴム等の軟質材料で変性した熱硬化性樹脂が好ましく、前記の熱可塑性樹脂、エラストマー、ゴムにより電極基材は加圧時に壊れにくくてより好ましい。

【００５２】高分子物質は、２３℃における圧縮弾性率が4,０００MPa以下であることが好ましく、２,０００MPa以下であるのがより好ましく、１,０００MPa以下であるのがさらに好ましい。圧縮弾性率の低い高分子物質は結着部にかかる応力を緩和して結着を外れにくくし、また、無機導電性物質にかかる応力を緩和して壊れにくくするためである。

【００５３】固体高分子型燃料電池は、カソード（空気極、酸素極）において、電極反応生成物としての水や、電解質を浸透した水が発生する。また、アノード（燃料極）においては、高分子電解質膜の乾燥防止のために燃料を加湿して供給する。これらの水の結露と滞留、水による高分子物質の膨潤が電極反応物を供給する際の妨げになるので、高分子物質の吸水率は低いほうがよい。好ましくは２０％以下、より好ましくは７％以下である。

【００５４】このような点から、電極基材には撥水性の高分子を含むことも好ましい実施態様である。特にポリテトラフルオロエチレン（ＰＴＦＥ）、テトラフルオロエチレン－ヘキサフルオロプロピレン共重合体（ＦＥＰ）、テトラフルオロエチレン－パーフルオロアルキルビニルエーテル共重合体（ＰＦＡ）などのフッ素原子を含有するポリマ（フッ素樹脂）が高い撥水性を有するため好ましく用いられる。電極基材を燃料電池用の集（給）電体として用いる場合は、撥水処理が必須であり、その際の撥水性の高分子は、電極基材を構成する導電性無機物質間の接着効果ももたらす。このことは、電極基材の強度、電気抵抗の点から有用である。ＰＴＦＥ、ＦＥＰ、ＰＦＡは、燃料電池集電体に求められる撥水性や耐酸化性が高く、ＰＴＦＥとＰＦＡは、電気抵抗が低い効果をもたらすためさらに好ましい。

【００５５】上記のような高分子物質の電極基材に対する含有率は、０．１～５０重量％の範囲にあるのが好ましい。電極基材の電気抵抗を低くするためには、高分子物質の含有率は少ないほうがよいが、０．１重量％未満ではハンドリングに耐える強度が不足し、無機導電性物質の脱落も多くなる。逆に、４０重量％を超えると電極基材の電気抵抗が増えてくるという問題が生じる。より好ましくは、１０～３０重量％の範囲である。

【００５６】電極基材に添加した高分子物質は、２００℃以上で焼成することも好ましい実施態様である。撥水処理に用いられる上記のフッ素樹脂は、融点以上に加熱することで、撥水性と結着性が向上する。また、フッ素樹脂以外の高分子物質においても、焼成により結着力が向上するほか、電気抵抗の低下、耐食性の向上が見られる。特にフッ素樹脂以外の高分子物質においては、耐酸化性に乏しい場合があり、燃料電池などの電気化学装置用電極として用いる際には、使用中に電極性能の低下をもたらす可能性がある。このため、電極作成時には結着剤として高分子物質物質を用い、電極として使用する前に焼成しておくことが好ましい。

【００５７】本発明の電極における電極触媒層は、特に限定されることなく公知のものを利用することが可能である。電極触媒層とは、電極反応に必要な触媒や電極活物質を含み、さらに好ましくは電極反応を促進する電子伝導やイオン伝導に寄与する物質も含んでいる。また電極活物質（酸化あるいは還元する物質）が気体の場合には、その気体が透過しやすい構造を有していることが必要であり、電極反応に伴う生成物質の排出も促す構造が必要である。本発明の電極を燃料電池に用いる場合には、電極活物質は水素あるいは酸素、触媒は白金などの貴金属粒子、電子伝導体はカーボンブラック、イオン伝導体はプロトン交換樹脂、反応生成物質は水である。電極触媒層は、触媒、電子伝導体、イオン伝導体が互いに接触して、活物質と反応生成物が効率よく出入りする構造が求められる。

【００５８】本発明の電極を燃料電池に用いる場合には、電極触媒層に含まれる触媒は公知の触媒を用いることができ、特に限定されるものではないが、白金、パラジウム、金、ルテニウム、イリジウムなどの貴金属触媒が好ましく用いられる。また、これらの貴金属触媒の合金、混合物など、２種以上の元素が含まれていても構わない。

【００５９】電極触媒層に含まれる電子伝導体（導電材）としては、特に限定されるものではないが、電子伝導性と耐蝕性の点から無機導電性物質が好ましく用いられる。なかでも、カーボンブラック、黒鉛質や炭素質の炭素材、あるいは金属や半金属が挙げられる。このような炭素材としては、オイルファーネスブラック、チャネルブラック、ランプブラック、サーマルブラック、アセチレンブラックなどのカーボンブラックが、電子電導性と比表面積の大きさから好ましいものである。オイルファーネスブラックとしては、キャボット社製バルカンＸＣ－７２、バルカンＰ、ブラックパールズ８８０、ブラックパールズ１１００、ブラックパールズ１３００、ブラックパールズ２０００、リーガル４００、ライオン社

製ケッチェンブラックＥＣ、三菱化学社製＃３１５０、＃３２５０などが挙げられ、アセチレンブラックとしては電気化学工業社製デンカブラックなどが挙げられる。またカーボンブラックのほか、天然の黒鉛、ピッチ、コークス、ポリアクリロニトリル、フェノール樹脂、フラン樹脂などの有機化合物から得られる人工黒鉛や炭素などがある。これらの炭素材の形態としては、粒子状のほか繊維状も用いることができる。また、これら炭素材を後処理加工した炭素材も用いることが可能である。このような炭素材の中でも、特に、キャボット社製のバルカンＸＣ－７２が電子電導性の点から好ましく用いられる。

【００６０】これら電子伝導体の添加量としては、要求される電極特性や用いられる物質の比表面積や電子抵抗などに応じて適宜決められるべきものであるが、電極触媒層中の重量比率として１～８０％が好ましく、２０～６０％がさらに好ましい。電子伝導体は、少ない場合は電子抵抗が低くなり、多い場合はガス透過性を阻害したり触媒利用率が低下するなど、いずれも電極性能を低下させる。

【００６１】電子伝導体は、触媒粒子と均一に分散していることが電極性能の点で好ましいものである。このため、触媒粒子と電子伝導体は予め塗液として良く分散しておき、この塗液を導電性中間層を設けた多孔質導電シート上に塗布する方法が好ましく用いられる。

【００６２】電極触媒層を燃料電池に用いる場合、触媒と電子伝導体とが一体化した触媒担持カーボンを用いることも好ましい実施態様である。この触媒担持カーボンを用いることにより、触媒の利用効率が向上し、低コスト化に寄与する。電極触媒層に触媒担持カーボンを用いた場合においても、さらに導電剤を添加することも可能である。このような導電剤としても、上述のカーボンブラックが好ましく用いられる。

【００６３】電極触媒層に用いられるイオン伝導体としては、公知のものが特に限定されることなく用いることが可能である。イオン伝導体としては、種々の有機・無機材料が公知であるが、燃料電池に用いる場合には、プロトン導電性を向上するスルホン酸基、カルボン酸基、リン酸基などのイオン交換基を有するポリマが好ましく用いられる。なかでも、フルオロアルキルエーテル側鎖とフルオロアルキル主鎖とから構成されるプロトン交換基を有するポリマが好ましく用いられる。たとえば、ＤｕＰｏｎｔ社製のＮａｆｉｏｎ、旭化成社製のＡｃｉｐｌｅｘ、旭硝子社製Ｆｌｅｍｉｏｎなどが好ましい。これらのイオン交換ポリマを溶液または分散液の状態で電極触媒層中に設けることができる。この際に、プロトン交換樹脂を溶解あるいは分散化する溶媒は特に限定されるものではないが、プロトン交換樹脂の溶解性の点から極性溶媒が好ましい。プロトン交換基を有する上述のフッ素原子を含むポリマや、エチレンやスチレンなどの他のポリマ、これらの共重合体やブレンドであっても構わない。

【００６４】イオン伝導体は、電極触媒層を作成する際に電極触媒粒子と電子伝導体を主たる構成物質とする塗液に予め添加し、均一に分散した状態で塗布することが電極性能の点から好ましいものであるが、電極触媒層を塗布した後にイオン導電体を塗布してもかまわない。電極触媒層にイオン導電体を塗布する方法としては、スプレーコート、刷毛塗り、ディップコート、ダイコート、カーテンコート、フローコートなど特に限定されるものではない。

【００６５】電極触媒層に含まれるイオン伝導体の量としては、要求される電極特性や用いられるイオン伝導体の電導度などに応じて適宜決められるべきものであり、特に限定されるものではないが、重量比で１～８０％が好ましく、５～５０％がさらに好ましい。イオン伝導体は、少ない場合はイオン伝導度が低く、多い場合はガス透過性を阻害する点で、いずれも電極性能を低下させる。

【００６６】電極触媒層には、上記の触媒、電子伝導体、イオン伝導体の他に、種々の物質を含んでいてもかまわない。特に電極触媒層中に含まれる物質の結着性を高めるために、上述のプロトン交換樹脂以外のポリマを含むことも好ましい実施態様である。このようなポリマとしては、フッ素原子を含有するポリマが挙げられ、特に限定されるものではないが、たとえば、ポリフッ化ビニル（ＰＶＦ）、ポリフッ化ビニリデン（ＰＶＤＦ）、ポリヘキサフルオロプロピレン（ＦＥＰ）、ポリテトラフルオロエチレン、ポリパーフルオロアルキルビニルエーテル（ＰＦＡ）など、あるいはこれらの共重合体、これらモノマ単位とエチレンやスチレンなどの他のモノマとの共重合体、さらには、ブレンドなども用いることができる。これらポリマの触媒層中の含有量としては、重量比で５～４０％が好ましい。ポリマ含有量が多すぎる場合、電子およびイオン抵抗が増大し電極性能が低下する。

【００６７】電極触媒層は、触媒－ポリマ複合体が三次元網目微多孔質構造を有することも好ましい実施態様である。触媒－ポリマ複合体は、触媒粒子を含んだポリマ複合体であって、この複合体が三次元網目微多孔質構造となっていることが特徴である。なお、「三次元網目微多孔構造」とは、触媒－ポリマ複合体が立体的に繋がった三次元状の網目構造をしている状態をいう。

【００６８】電極触媒層が三次元網目微多孔質構造を有している場合、その微多孔径が０．０５～５μｍであることが好ましい。より好ましくは、０．１～１μｍである。微多孔径は、走査型電子顕微鏡（ＳＥＭ）などで、表面を撮影した写真から、２０個以上好ましくは１００個以上の平均から求めることができ、通常は１００個で測定できる。湿式凝固法によって製造された場合の本発

明の微多孔質構造の触媒層は、微多孔径の分布が広いのでできるだけ多くの孔径の平均をとることが好ましい。

【００６９】三次元網目微多孔質構造の空孔率は、１０～９５％であることが好ましい。より好ましくは５０～９０％である。空孔率は、触媒層全体積から触媒－ポリマ複合体の占める体積を減じたものを触媒層全体積で除した百分率（％）である。触媒層は、電極基材、プロトン交換膜、それ以外の基材に塗布した後に湿式凝固を行うが、触媒層を単独で空孔率を求めることが困難な場合には、電極基材、プロトン交換膜、それ以外の基材の空孔率を予め求めておき、これら基材と触媒層とを含む空孔率を求めた後に、触媒層単独での空孔率を求めることも可能である。

【００７０】電極触媒層は、特に湿式凝固法に得られた三次元網目微多孔質構造のものは、空孔率が大きくガス拡散性や生成水の排出が良好であり、かつ電子伝導性やプロトン伝導性も良好である。従来の多孔化では、触媒粒子径や添加ポリマの粒子径を増大させたり、造孔剤を用いて空孔を形成するなどが行われているが、このような多孔化方式では触媒担持カーボン間やプロトン交換樹脂間の接触抵抗が電極触媒層に比べて大きくなってしまう。それに対して、湿式凝固法による三次元網目微多孔質構造では、触媒担持カーボンを含んだポリマ複合体が三次元網目状になっているので、このポリマ複合体を電子やプロトンが伝導しやすく、さらに微多孔質構造のためガス拡散性や生成水の排出も良好な構造となっている。

【００７１】電極触媒層が三次元微多孔質構造を有している場合においても、触媒や電子伝導体、イオン伝導体に用いられる物質は従来と同様の物質を用いることが可能である。ただし、三次元網目微多孔質構造を有する電極触媒層を作成する際に湿式凝固法によることが好ましい。従って、前記の場合、この湿式凝固法に適したポリマを用いることが好ましく、また、触媒粒子を良く分散し、燃料電池内の酸化－還元雰囲気で劣化しないポリマを用いるが好ましい。このようなポリマとしては、フッ素原子を含有するポリマが挙げられ、特に限定されるものではないが、たとえば、ポリフッ化ビニル（ＰＶＦ）、ポリフッ化ビニリデン（ＰＶＤＦ）、ポリヘキサフルオロプロピレン（ＦＥＰ）、ポリパーフルオロアルキルビニルエーテル（ＰＦＡ）など、あるいはこれらの共重合体、これらモノマ単位とエチレンやスチレンなどの他のモノマとの共重合体（例えば、ヘキサフルオロプロピレン－フッ化ビニリデン共重合体）、さらには、ブレンドなども用いることができる。

【００７２】この中でも、ポリフッ化ビニリデン（ＰＶＤＦ）やヘキサフルオロプロピレン－フッ化ビニリデン共重合体は、非プロトン性極性溶媒を用い、プロトン性極性溶媒などを凝固溶媒とする湿式凝固法により、三次元網目微多孔質構造を有する触媒－ポリマ複合体が得られる点で、特に好ましいポリマである。これらポリマの溶媒としてはＮ－メチルピロリドン（ＮＭＰ）、ジメチルホルムアミド（ＤＭＦ）、ジメチルアセトアミド（ＤＭＡＣ）、プロピレンカーボネート（ＰＣ）、ジメチルイミダゾリジノン（ＤＭＩ）などが挙げられ、凝固溶媒としては水や、メタノール、エタノール、イソプロパノールなどの低級アルコール類などのほか、酢酸エチルや酢酸ブチルなどのエステル類、芳香族系あるいはハロゲン系の種々の有機溶剤が用いられる。

【００７３】触媒－ポリマ複合体のポリマとしては、上記のポリマに加えて、プロトン伝導性を向上させるためにプロトン交換基を有するポリマも好ましいものである。このようなポリマに含まれるプロトン交換基としては、スルホン酸基、カルボン酸基、リン酸基などがあるが特に限定されるものではない。また、このようなプロトン交換基を有するポリマも、特に限定されることなく選ばれるが、フルオロアルキルエーテル側鎖とフルオロアルキル主鎖とから構成されるプロトン交換基を有するポリマが好ましく用いられる。たとえば、DuPont社製のNafionなども好ましいものである。また、プロトン交換基を有する上述のフッ素原子を含有するポリマや、エチレンやスチレンなどの他のポリマ、これらの共重合体やブレンドであっても構わない。

【００７４】Nafionのポリマ溶液は、市販のNafion膜を非プロトン性極性溶媒に溶かしても良いし、Aldrich社製の水－メタノール－イソプロパノール混合溶媒のNafion溶液、あるいはこのNafion溶液を溶媒置換したもの用いても良い。この場合、湿式凝固の際の凝固溶媒は、Nafion溶液の溶媒により適宜決められるべきものであるが、Nafion溶液の溶媒が非プロトン性極性溶媒である場合には、凝固溶媒としては水やアルコール類、エステル類のほか、種々の有機溶媒などが好ましく、水－メタノール－イソプロパノール混合溶媒などの場合には、酢酸ブチルなどのエステル類、種々の有機溶媒が好ましく用いられる。

【００７５】触媒－ポリマ複合体に用いられるポリマは、上記のフッ素原子を含有するポリマやプロトン交換基を含むポリマを共重合あるいはブレンドして用いることも好ましいものである。特にポリフッ化ビニリデン、ポリ（ヘキサフルオロプロピレン－フッ化ビニリデン）共重合体などと、プロトン交換基にフルオロアルキルエーテル側鎖とフルオロアルキル主鎖を有するNafionなどのポリマを、ブレンドすることは電極性能の点から好ましいものである。

【００７６】触媒－ポリマ複合体の主たる成分は触媒担持カーボンとポリマであり、それらの比率は必要とされる電極特性に応じて適宜決められるべきもので特に限定されるものではないが、触媒担持カーボン／ポリマの重量比率で５／９５～９５／５が好ましく用いられる。特に固体高分子型燃料電池用電極触媒層として用いる場合

には、触媒担持カーボン／ポリマ重量比率で４０／６０～８５／１５が好ましいものである。

【００７７】触媒－ポリマ複合体には、種々の添加物を加えることも好ましい実施態様である。たとえば、電子伝導性向上のための炭素などの導電剤や、結着性向上のためのポリマ、三次元網目微多孔質構造の孔径を制御する添加物などがあるが、特に限定されることなく用いることができる。これら添加物の添加量としては、触媒－ポリマ複合体に対する重量比率として０．１～５０％が好ましく、１～２０％がさらに好ましい。

【００７８】三次元網目微多孔質構造を有する触媒－ポリマ複合体の製造方法としては、湿式凝固法によるものが好ましい。この湿式凝固法は、触媒－ポリマ溶液組成物を塗布した後に、この塗布層をポリマに対する凝固溶媒と接触させて、触媒－ポリマ溶液組成物の凝固析出と溶媒抽出とが同時に行なわれる。

【００７９】この触媒－ポリマ溶液組成物は、ポリマ溶液中に触媒担持カーボンが均一に分散したものである。触媒担持カーボンとポリマは前述のものが好ましく用いられる。ポリマを溶かす溶媒については、用いられるポリマに応じて適宜決められるべきもので、特に限定されるものではない。ポリマ溶液は触媒担持カーボンを良く分散していることが重要である。分散状態が悪い場合には、湿式凝固の際に、触媒担持カーボンとポリマとが複合体を形成することができず好ましくない。

【００８０】塗布方法については、触媒－ポリマ溶液組成物の粘度や固形分などに応じた塗布方法が選択され、特に限定されるべきものではないが、ナイフコーター、バーコーター、スプレー、ディップコーター、スピンコーター、ロールコーター、ダイコーター、カーテンコーターなどの一般的な塗布方法が用いられる。

【００８１】一方、ポリマを湿式凝固させる凝固溶媒についても特に限定されるものではないが、用いられるポリマを凝固析出しやすく、かつポリマ溶液の溶媒と相溶性がある溶媒が好ましい。湿式凝固が実際に行われる凝固溶媒との接触方法についても、特に限定されるものではないが、凝固溶媒に基材ごと浸漬する、塗布層のみを凝固溶媒の液面に接触させる、凝固溶媒を塗布層にシャワリングあるいはスプレーする、など特に限定されるものではない。

【００８２】この触媒－ポリマ溶液組成物が塗布される基材については、電極基材あるいは固体電解質の何れにおいても塗布、その後に湿式凝固を行うことが可能であるが、電極基材に塗布の直後に湿式凝固を行うことで電極基材への触媒層の浸み込みを抑制することが可能となり、本発明の好ましい実施態様となる。また、電極基材や固体電解質以外の基材（転写基材）に塗布し、その後に湿式凝固を行い、三次元網目微多孔質構造を作成した後に、この触媒層を電極基材や固体電解質に転写あるいは挟持させても良い。この場合の転写基材としては、ポリテトラフルオロエチレン（ＰＴＦＥ）のシート、あるいは表面をフッ素やシリコーン系の離型剤処理したガラス板や金属板なども用いられる。

【００８３】本発明の電極は、電極基材の中に電極触媒層が浸み込んでいる複合層を２０μｍ以下の厚さにすることによって、有効利用されない無駄な触媒低減することを目的とするものであり、その製造方法は特に限定されるものではない。電極基材に多孔質導電シートを用いる場合、電極触媒層塗液が電極基材に浸み込みやすいため、本発明の電極とするためには浸み込まない工夫が必要である。例えば、電極触媒層塗液の粘度を高くする、電極基材および含まれる高分子材料と電極触媒層塗液の表面エネルギーの差を大きくするなどの方法がある。

【００８４】電極触媒層塗液の粘度を高くすると、多孔質導電シートへの浸み込みが抑制される。粘度を高めるには、触媒層塗液の溶媒以外の固形分比率を高くする、触媒層塗液に含まれる高分子物質の分子量を高くする、触媒層塗液に種々の増粘剤を添加するなどの方法がある。増粘剤の例としては、グリセリンなどの多価アルコール類、オクタノールなどの高級アルコール類、カルボキシメチルセルロース、ヒドロキシプロピルセルロースなどのセルロース類、ポリビニルアルコール、ポリビニルピロリドンなどの高分子化合物、アセチレンブラック、ケッチェンブラックなどのカーボンブラック類などが好ましいが、特に限定されるものではない。

【００８５】電極基材および含まれるポリマと電極触媒層塗液との表面エネルギー差を利用する場合は、電極基材と電極触媒層塗液との静的接触角が５０°以上（より好ましくは７０°以上）とすることで、浸み込みを抑制することが可能である。電極基材は、燃料電池に用いる場合は撥水処理を行うためにフッ素樹脂を含み、表面自由エネルギーが低くなっている。このため、表面自由エネルギーの大きな溶媒を含む電極触媒層塗液を用いることで、静的接触角が増大し浸み込み抑制がなされる。電極触媒層にはイオン伝導体としてプロトン交換樹脂が含まれている。このためイオン交換樹脂を含む触媒層塗液は水を含んでおり、このような場合、静的接触角が大きくなることで浸み込み抑制がなされる。電極基材にフッ素樹脂が含まれる場合には、水のほかＮ－メチルピロリドンを電極触媒層塗液の溶媒に用いると、静的接触角が大きくなり浸み込み抑制がなされる。静的接触角の測定は、基材上に触媒層塗液をマイクロシリンジで一滴落とし、側面から顕微鏡で測定するという、一般的な測定法でよい。

【００８６】本発明の電極は、固体電解質層とを組み合わせることにより膜－電極複合体（ＭＥＡ：Membrane Electrode Assembly）とすることも好ましい実施態様である。

【００８７】固体電解質層を構成している固体電解質としては、通常の燃料電池に用いられる固体電解質であれ

は特に限定されるものではないが、プロトン交換膜が本発明の燃料電池性能を発現するうえで好ましく用いられる。プロトン交換膜のプロトン交換基としては、スルホン酸基、カルボン酸基、リン酸基など特に限定されるものではない。

【００８８】このプロトン交換膜は、上記のプロトン交換基、特にスルホン酸基を有する、スチレン－ジビニルベンゼン共重合体などの炭化水素系と、フッ素原子含有ポリマ、特にフルオロアルキルエーテル側鎖とフルオロアルキル主鎖とから構成される共重合体のパーフルオロ系に大別され、燃料電池が用いられる用途や環境に応じて適宜選択されるべきものであるが、フッ素原子含有ポリマ、特にパーフルオロ系が燃料電池寿命の点から好ましいものである。また、部分的にフッ素原子置換した部分フッ素膜も好ましく用いられる。パーフルオロ膜では、DuPont社製Nafion、旭化成製Aciplex、旭硝子製Flemion、ジャパンゴアテックス社製Goa-selectなどが例示され、部分フッ素膜では、トリフルオロスチレンスルホン酸の重合体やポリフッ化ビニリデンにスルホン酸基を導入したものなどがある。また、プロトン交換膜は１種のポリマばかりでなく、２種以上のポリマの共重合体やブレンドポリマ、２種以上の膜を貼り合わせた複合膜、プロトン交換膜を不織布や多孔フィルムなどで補強した膜なども用いることができる。

【００８９】膜－電極複合体の製造方法としては、特に限定されるものではない。一般的には、電極基材上に電極触媒層を設けて電極を作成し、この電極をプロトン交換膜などの固体電解質と接合するが、この接合条件についても電極触媒層あるいは電気化学装置の特性に応じて適宜決められるべきものである。

【００９０】本発明の電極の特性を活かす上では、電極基材と電極触媒層とから構成される電極を予め２枚作成し、これらの２枚の電極の間にプロトン交換膜を各電極の電極触媒層側がプロトン交換膜に対面するように配置し、前記２枚の電極で該プロトン交換膜を挟持させて接合することによるＭＥＡの製造方法が好ましいものである。この接合は加温プレスとなるが、この条件についても特に限定されるものではない。一般的には、プレス温度は２０℃～２００℃、プレス圧力は１ＭＰａ～２０ＭＰａである。

【００９１】その他の膜-電極複合体製造方法としては、プロトン交換膜の表裏両面に前記電極触媒層を設ける工程（工程Ａ）、該電極触媒層の両外側面に電極基材を設ける工程（工程Ｂ）をこの順で行うことも好ましい製造方法である。この方法は、電極基材への触媒層塗布を行わないため、基材への触媒層浸み込みを抑制する点で本発明の電極からなるＭＥＡを作成可能とする方法である。

【００９２】特に、電極触媒層塗液をプロトン交換膜上に塗工し、その後に電極基材を設けるＭＥＡ製造方法も好ましいものである。この場合においては、触媒塗液を塗布するプロトン交換膜は水や有機溶媒により膨潤しやすいため、触媒層塗液に用いる溶媒は、プロトン交換膜を膨潤しにくい溶媒を選択する必要がある。しかしながら、触媒層塗液にはプロトン交換樹脂が含まれおり、このプロトン交換樹脂を溶解する溶媒ではプロトン交換膜を膨潤あるいは溶かしてしまうことになる。このため、触媒層塗液においては、含まれるプロトン交換樹脂を溶解することなく、エマルジョンなどの形態で分散させる溶媒を用いることが好ましい。例えば、プロトン交換樹脂溶液を溶媒除去、乾燥、粉砕し、得られたプロトン交換樹脂粉末と触媒担持カーボンとをプロトン交換膜を膨潤させない溶媒中で混合・分散する方法、あるいは、プロトン交換樹脂溶液と触媒担持カーボンとの分散液を溶媒除去、乾燥、粉砕し、得られた粉末をプロトン交換樹脂と膨潤しない溶媒に再分散する方法、などが挙げられるが特に限定されるものではない。

【００９３】さらに、上記の工程Ａにおいて、電極触媒塗液を電極基材やプロトン交換膜以外の転写基材上に塗布して電極触媒層を形成し、これをプロトン交換膜上に転写することも好ましいＭＥＡ製造方法である。この際の転写基材としては、各種の樹脂、あるいはＰＴＦＥ、ＰＦＡ、ＦＥＰなどのフッ素樹脂からなるシートやフィルムなどの転写基材や、ガラス板などを用いることが可能である。特にシートやフィルムに電極触媒層を塗工して、それをプロトン交換膜とロールプレスすることで、プロトン交換膜上に転写することが可能である。

【００９４】また、上記工程Ｂにおいて、電極基材を構成する物質をプロトン交換膜に塗工することで電極基材を設けることも好ましいＭＥＡ製造方法である。電極基材を構成する無機導電性繊維や粒子を液状あるいは固体状で、電極触媒層を設けたプロトン交換膜に吹き付けることによりＭＥＡが作成される。特に、電極基材を構成する無機導電性物質が炭素短繊維の場合には、これとフッ素原子含有ポリマを含む分散液を予め作成し、この分散液を電極触媒層を設けたプロトン交換膜上に吹き付けることにより塗工することも好ましい。

【００９５】本発明の電極基材と電極触媒層とからなる電極、あるいは該電極と固体電解質膜からなる膜－電極複合体（ＭＥＡ）は、種々の電気化学装置に適応することができる。なかでも燃料電池や水電解層が好ましく、さらに燃料電池のなかでも固体高分子型燃料電池に好適である。燃料電池には、水素を燃料とするものとメタノールなどの炭化水素を燃料とするものがあるが、特に限定されることなく用いることができる。

【００９６】さらに、本発明の電極触媒層を用いた燃料電池の用途としては、特に限定されることなく考えられるが、固体高分子型燃料電池において有用な用途である移動体の電力供給源が好ましいものである。特に、乗用車、バス、トラックなどの自動車や船舶、鉄道なども好

ましい移動体である。

【００９７】

【実施例】以下本発明の詳細につき実施例を用いてさらに説明する。

【００９８】実施例１

（１）電極基材の作成

多孔質導電シートとしてカーボンペーパー（東レ製ＴＧＰ－Ｈ－０６０）を用い、これをＰＴＦＥ分散液（ダイキン工業製：ポリフロンＴＦＥ　Ｄ－１、ディスパージョン平均粒径０．２－０．４μｍ、６０重量％、水溶液）に含浸し、乾燥後、３７０℃にて焼成した。ＰＴＦＥの付き量は２０重量％であった。

【００９９】（２）触媒層塗液の調製

市販のAldrich社製Nafion溶液（５重量％）を濃縮して１５重量％とした。この濃縮Ｎａｆｉｏｎ溶液１０ｇに触媒担持カーボン（触媒：Ｐｔ、カーボン：Cabot社製VulcanXC-72、白金担持量：５０ｗｔ％）３ｇを加え、良く撹拌して触媒－ポリマ組成物からなる触媒層塗液を調製した。

【０１００】（３）電極触媒層塗液の塗布、乾燥による電極の作成

前記（１）で作成した多孔質導電シート上に、前記（２）で調製した触媒層塗液を塗布、乾燥し、電極基材と電極触媒層とから構成される電極を作成した。得られた電極は、白金付き量０．５ｍｇ／ｃｍ²、Nafionの付き量０．３ｍｇ／ｃｍ²であった。

【０１０１】この電極の断面ＳＥＭ写真を図１（１）に、またＸ線マイクロアナリシスによる白金の分布を図１（３）に示す。電極触媒層が電極基材へ浸み込んだ混合層の厚さは１０μｍ、混合層を含まない純触媒層は１５μｍであった。

【０１０２】比較例１

（１）電極基材の作成

実施例１と同様に、多孔質導電シートとしてカーボンペーパー（東レ製ＴＧＰ－Ｈ－０６０）を用い、これをＰＴＦＥ分散液（ダイキン工業製：ポリフロンＰＴＦＥディスパージョン）に含浸し、乾燥後、３７０℃にて焼成した。ＰＴＦＥの付き量は２０重量％であった。

【０１０３】（２）触媒層塗液の調製

市販のAldrich社製Nafion溶液（５重量％）をそのまま用いて、触媒担持カーボン（触媒：Ｐｔ、カーボン：Cabot社製VulcanXC-72、白金担持量：５０ｗｔ％）を加え、良く撹拌して触媒－ポリマ組成物からなる触媒層塗液を調製した。

【０１０４】（３）電極触媒層塗液の塗布、乾燥による電極の作成

前記（１）で作成した多孔質導電シート上に、前記（２）で調製した触媒層塗液を塗布、乾燥し、電極基材と電極触媒層とから構成される電極を作成した。得られた電極は、白金付き量０．５ｍｇ／ｃｍ²、Nafionの付き量０．３ｍｇ／ｃｍ²であった。

【０１０５】この電極の断面ＳＥＭ写真からは、電極触媒層が電極基材へ浸み込んだ混合層の厚さは、４０μｍであった。

【０１０６】実施例２

（１）電極基材の作成

多孔質導電シートとしてカーボンペーパー（東レ製ＴＧＰ－Ｈ－０６０）を用い、これをＰＦＡ分散液（ダイキン工業製：ネオフロンＰＦＡ　ＡＤ－２ＣＲ）に含浸し、乾燥後、３２０℃にて焼成した。ＰＦＡの付き量は２０重量％であった。

【０１０７】（２）触媒層塗液の調製

市販のAldrich社製Nafion溶液（５重量％）に増粘剤としてカルボキシメチルセルロースを０．１重量％添加した。これに、触媒担持カーボン（触媒：Ｐｔ、カーボン：Cabot社製VulcanXC-72、白金担持量：５０ｗｔ％）を加え、良く撹拌して触媒－ポリマ組成物からなる触媒層塗液を調製した。

【０１０８】（３）電極触媒層塗液の塗布、乾燥による電極の作成

前記（１）で作成した多孔質導電シート上に、前記（２）で調製した触媒層塗液を塗布、乾燥し、電極基材と電極触媒層とから構成される電極を作成した。得られた電極は、白金付き量０．５ｍｇ／ｃｍ²、Nafionの付き量０．３ｍｇ／ｃｍ²であった。

【０１０９】この電極の断面ＳＥＭ写真からは、電極触媒層が電極基材へ浸み込んだ混合層の厚さは、１０μｍであった。

【０１１０】実施例３

（１）電極基材の作成

実施例２と同様に、多孔質導電シートとしてカーボンペーパー（東レ製ＴＧＰ－Ｈ－０６０）を用い、これをＰＦＡ分散液（ダイキン工業製：ネオフロンＰＦＡディスパージョン）に含浸し、乾燥後、３２０℃にて焼成した。ＰＦＡの付き量は２０重量％であった。

【０１１１】（２）触媒層塗液の調製

市販のAldrich社製Nafion溶液（５重量％）を濃縮しながらＮ－メチルピロリドンを添加して、溶媒置換を行った。得られたNafion溶液は１０重量％であった。これに触媒担持カーボン（触媒：Ｐｔ、カーボン：Cabot社製VulcanXC-72、白金担持量：５０ｗｔ％）を加え、良く撹拌して触媒－ポリマ組成物からなる触媒層塗液を調製した。

【０１１２】（３）触媒－ポリマ組成物の塗布、乾燥による電極触媒層の作成

前記（１）で作成した多孔質導電シート上に、前記（２）で調製した触媒層塗液を塗布、乾燥し、電極基材と電極触媒層とから構成される電極を作成した。得られた電極は、白金付き量０．５ｍｇ／ｃｍ²、Nafionの付き量０．３ｍｇ／ｃｍ²であった。

【０１１３】この電極基材上に触媒層塗液を一滴静置した際の静的接触角は、９０°であった。

【０１１４】この電極の断面ＳＥＭ写真からは、電極触媒層が電極基材へ浸み込んだ混合層の厚さは、１５μｍであった。

【０１１５】実施例４

（１）電極基材の作成

実施例１と同様に、多孔質導電シートとしてカーボンペーパー（東レ製ＴＧＰ－Ｈ－０６０）を用い、これをＰＴＦＥ分散液（ダイキン工業製：ポリフロンＰＴＦＥディスパージョン）に含浸し、乾燥後、３７０℃にて焼成した。ＰＴＦＥの付き量は２０重量％であった。

【０１１６】（２）触媒層塗液の調製

市販のAldrich社製Nafion溶液（５重量％）を濃縮して１０重量％とした。これに触媒担持カーボン（触媒：Ｐｔ、カーボン：Cabot社製VulcanXC-72、白金担持量：５０ｗｔ％）を加え、良く攪拌して触媒－ポリマ組成物からなる触媒層塗液を調製した。

【０１１７】（３）電極触媒層の塗布、湿式凝固、乾燥による微多孔構造電極の作成

前記（１）で作成した多孔質導電シート上に、前記（２）で調製した触媒層塗液を塗布後、直ちに酢酸ブチルに浸漬、乾燥することにより、電極基材と微多孔構造電極触媒層とから構成される電極を作成した。得られた電極は、白金付き量０．５ｍｇ／ｃｍ²、Nafionの付き量０．３ｍｇ／ｃｍ²であった。

【０１１８】この電極の断面ＳＥＭ写真からは、電極触媒層が電極基材へ浸み込んだ混合層の厚さは、１０μｍであった。

【０１１９】実施例５

（１）多孔質導電シートの作成

長さ１２ｍｍにカットされたＰＡＮ系炭素繊維の短繊維と膨張黒鉛粉末（東洋炭素（株）製、かさ密度０．１４ｇ／ｃｍ³、平均粒径１００乃至２００μｍ）を、重量比で１：１に混合し、ナトリウムカルボキシメチルセルロース水溶液中に分散した。この分散液を用い、炭素繊維の短繊維に膨張黒鉛粉末が付着したシートを金網上に抄造した。水分を除去する目的で、シートを２枚の濾紙に挟み軽く加圧した。その後、濾紙を外してシートを乾燥した。乾燥後、シートをロールプレスし、多孔質導電シートを製造した。得られたシートは８０ｇ／ｍ²であった。

【０１２０】（２）電極基材の作成

前記（１）で作成した多孔質導電シートを空気中で２００℃、３０分の熱処理を行った後、ＰＦＡディスパージョン（ネオフロンＰＦＡディスパージョン、ダイキン工業株式会社製）を含浸し、２枚の濾紙に挟んで軽く加圧、乾燥した。さらにこのシートを、１４．７ｋＰａ（０．１５ｋｇｆ／ｃｍ²）で加圧しながら４００℃、３時間の熱処理を行い、多孔質導電シートを製造した。ＰＦＡの付き量は１５重量％であった。

【０１２１】（３）電極触媒層の作成

市販のAldrich社製Nafion溶液（５重量％）を濃縮しながらＮ－メチルピロリドンを添加して、溶媒置換を行った。得られたNafion溶液は１０重量％であった。これに触媒担持カーボン（触媒：Ｐｔ、カーボン：Cabot社製VulcanXC-72、白金担持量：５０ｗｔ％）を加え、良く攪拌して触媒－ポリマ組成物からなる触媒層塗液を調製した。

【０１２２】（４）電極触媒層塗液の塗布、乾燥による電極の作成

前記（２）で作成した多孔質導電シート上に、前記（３）で調製した触媒層塗液を塗布、乾燥し、電極基材と電極触媒層とから構成される電極を作成した。得られた電極は、白金付き量０．５ｍｇ／ｃｍ²、Nafionの付き量０．３ｍｇ／ｃｍ²であった。

【０１２３】この電極基材上に触媒層塗液を一滴静置した際の静的接触角は、９０°であった。

【０１２４】この電極の断面ＳＥＭ写真からは、電極触媒層が電極基材へ浸み込んだ混合層の厚さは、１５μｍであった。

【０１２５】実施例６

（１）電極の作成

実施例２と同様に電極を作成した。

【０１２６】（２）膜－電極複合体（ＭＥＡ）

前記（１）において作成した電極を２枚用意し、プロトン交換膜（ＤｕＰｏｎｔ社製ナフィオン１１２）の両側から電極触媒層面を対向させて挟持した。これを１５０℃、１５０ＭＰａでホットプレスを行い、ＭＥＡを作成した。

【０１２７】このＭＥＡの断面をＳＥＭ観察したところ、電極触媒層が電極基材へ浸み込んだ混合層の厚さは１０μｍであった。

【０１２８】（３）ＭＥＡの燃料電池性能評価

前記（２）において作成したＭＥＡは、電流－電圧（Ｉ－Ｖ）測定により燃料電池性能評価を行った。評価セル温度は７０℃、アノード（燃料）ガスを水素、カソード（酸化）ガスを空気、ガス圧力は常圧において最高出力４５０ｍＷ／ｃｍ²であり良好な性能を示した。

【０１２９】比較例２

比較例１において作成した電極を用い、実施例６と同様にＭＥＡを作成した。

【０１３０】このＭＥＡ断面のＳＥＭ観察では、電極触媒層が電極基材に浸み込んだ混合層の厚さは３０μであった。

【０１３１】さらに、このＭＥＡを実施例６と同じ条件でＩ－Ｖ測定したが、最高出力２５０ｍＷ／ｃｍ²と実施例６に比べて低出力であり、劣った性能であった。

【０１３２】実施例７

（１）電極触媒層塗液の作成

市販のプロトン交換樹脂溶液（Aldrich社製Nafion溶液）を凍結乾燥、凍結粉砕を行い、プロトン交換樹脂粉末を作成した。この粉末１．５ｇと触媒担持カーボン（触媒；Ｐｔ、カーボン；Cabot社製VulcanXC-72、白金担持量；５０ｗｔ％）３ｇを酢酸ブチル１０ｇに加えて、混合・分散を充分に行い、触媒層塗液を作成した。

【０１３３】（２）ＭＥＡの作成
前記（１）において作成した電極触媒層塗液を用い、市販のプロトン交換膜（ＤｕＰｏｎｔ社製ナフィオン１１２）の両面に塗布、乾燥した。この両側から、電極基材としてカーボンクロス（Ｅ－ＴＥＫ社製ＥＬＡＴ）を狭持させてＭＥＡを作成した。

【０１３４】得られたＭＥＡの断面ＳＥＭ観察を行ったところ、電極触媒層が電極基材へ浸み込んだ複合層の厚さは５μｍであった。

【０１３５】（３）ＭＥＡの燃料電池性能評価
前記（２）において作成したＭＥＡは、電流－電圧（ｉ－Ｖ）測定により燃料電池性能評価を行った。評価セル温度は７０℃、アノード（燃料）ガスを水素、カソード（酸化）ガスを酸素、ガス圧力は常圧において最高出力８００ｍＷ／ｃｍ²であり良好な性能を示した。

【０１３６】実施例８
（１）電極触媒層塗液の作成
市販のプロトン交換樹脂溶液（Aldrich社製Nafion溶液５％）１０ｇに触媒担持カーボン（触媒；Ｐｔ、カーボン；Cabot社製VulcanXC-72、白金担持量；５０ｗｔ％）を１ｇ加えて、充分に混合・分散を行った後、溶媒を乾燥除去、粉砕して粉末を得た。この粉末にジオキサン８ｇを加えて、混合・分散を充分に行い、触媒層塗液を作成した。

【０１３７】（２）ＭＥＡの作成
実施例７（２）と同様に、前記（１）において作成した電極触媒層塗液と実施例５（１）で作成した電極基材を用いてＭＥＡを作成した。得られたＭＥＡの断面ＳＥＭ観察からは、混合層の厚さは５μｍであった。

【０１３８】（３）ＭＥＡの燃料電池性能評価
前記（２）において作成したＭＥＡは、電流－電圧（ｉ－Ｖ）測定により燃料電池性能評価を行った。評価セル温度は８０℃、アノード（燃料）ガスを水素、カソード（酸化）ガスを空気、ガス圧力は０．２ＭＰａにおいて最高出力８５０ｍＷ／ｃｍ²であり良好な性能を示した。

【０１３９】実施例９
（１）電極基材の作成
実施例５（１）（２）と同様に電極基材を作成した。

【０１４０】（２）電極触媒層の作成
市販のAldrich社製Nafion溶液（５重量％）に触媒担持カーボン（触媒；Ｐｔ、カーボン；Cabot社製VulcanXC-72、白金担持量；５０ｗｔ％）を加え、良く攪拌して触媒－ポリマ組成物からなる触媒層塗液を調製した。この触媒層塗液を厚さ１００μｍのテフロンシート上に、塗布、乾燥し、電極触媒層を作成した。得られた電極触媒層は、白金付き量０．５ｍｇ／ｃｍ²、Nafionの付き量０．３ｍｇ／ｃｍ²であった。

【０１４１】（３）プロトン交換膜への電極触媒層の転写
前記（２）において作成した電極触媒層を２枚用意し、プロトン交換膜（ＤｕＰｏｎｔ社製ナフィオン１１２）の両側から電極触媒層面を対向させて狭持した。これをロールプレスして、プロトン交換膜へ電極触媒層を転写し、電極触媒層つきプロトン交換膜を作成した。

【０１４２】（４）ＭＥＡの作成
前記（３）で作成した電極触媒層つきプロトン交換膜を用い、前記（１）で作成した電極基材２枚を両側から狭持させてＭＥＡを作成した。このＭＥＡの断面ＳＥＭ観察からは、複合層の厚さは５μｍであった。

【０１４３】（５）ＭＥＡの性能評価
前記（４）において作成したＭＥＡは、電流－電圧（ｉ－Ｖ）測定により燃料電池性能評価を行った。評価セル温度は６０℃、アノード（燃料）ガスを水素、カソード（酸化）ガスを空気、ガス圧力は常圧において最高出力３５０ｍＷ／ｃｍ²であり良好な性能を示した。

【０１４４】実施例１０
（１）電極触媒層塗液の作成
市販のプロトン交換樹脂溶液（Aldrich社製Nafion溶液）を凍結乾燥、凍結粉砕を行い、プロトン交換樹脂粉末を作成した。この粉末１．５ｇと触媒担持カーボン（触媒；Ｐｔ、カーボン；Cabot社製VulcanXC-72、白金担持量；５０ｗｔ％）３ｇを酢酸ブチル１０ｇに加えて、混合・分散を充分に行い、触媒層塗液を作成した。

【０１４５】（２）電極基材塗液の作成
長さ１２ｍｍにカットされたＰＡＮ系炭素繊維の短繊維と膨張黒鉛粉末（東洋炭素（株）製、かさ密度０．１４ｇ／ｃｍ³、平均粒径１００乃至２００μｍ）を、重量比で１：１に混合し、ＰＦＡディスパージョン（ネオフロンＰＦＡディスパージョン、ダイキン工業株式会社製）に充分に混合・分散し、電極基材塗液を作成した。ＰＦＡの付き量は１５重量％であった。

【０１４６】（３）ＭＥＡの作成
前記（１）において作成した電極触媒層塗液を用い、市販のプロトン交換膜（ＤｕＰｏｎｔ社製ナフィオン１１２）の両面に塗布、乾燥した。この両側から、前記（２）で作成した電極触媒層塗液を塗布、乾燥してＭＥＡを作成した。

【０１４７】得られたＭＥＡの断面ＳＥＭからは、混合層の厚さは５μｍであった。

【０１４８】（４）ＭＥＡの性能評価
前記（３）において作成したＭＥＡは、電流－電圧（ｉ－Ｖ）測定により燃料電池性能評価を行った。評価セル温度は７０℃、アノード（燃料）ガスを水素、カソード

（酸化）ガスを酸素、ガス圧力は高圧において最高出力５００mW／cm²であり良好な性能を示した。

【０１４９】

【発明の効果】本発明により触媒複み込みの少ない電極が得られ、したがって、触媒の利用効率が向上し．触媒量低減による低コスト化電極が得られる。

【０１５０】本発明の電極は、膜-電極複合体（ＭＥＡ）に適用されるほか、通常の電気化学装置、特に固体高分子型燃料電池にも適用され、この燃料電池を用いた移動体や自動車にも適用されるものである。

【図面の簡単な説明】

【図１】　本発明の実施例の断面図である。

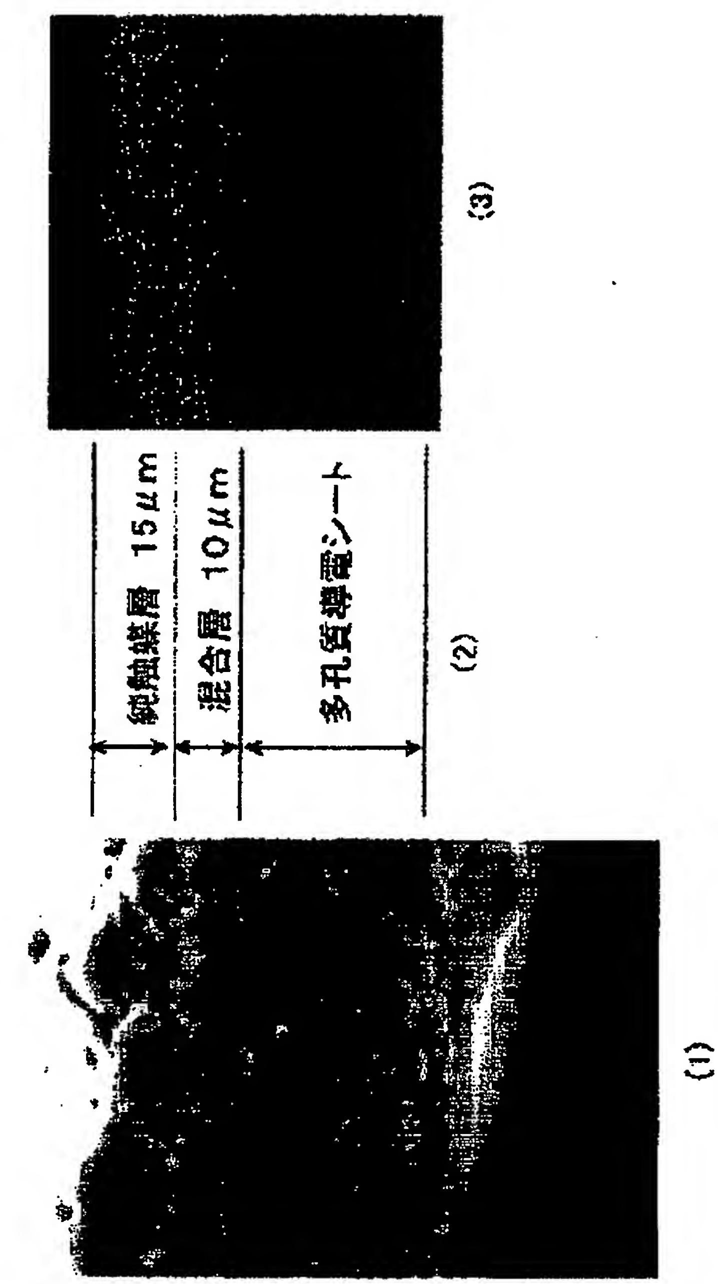
【符号の説明】

１：本発明実施例の断面の走査型電子顕微鏡写真

２：断面区分表示

３：本発明実施例の断面のＸ線マイクロアナリシスによる白金の分布図

【図1】



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EE05 EE08 EE18 HH03
5H026 AA06 BB04 CX03 CX05 EE02
EE05 EE19 HH03

* NOTICES *

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1.This document has been translated by computer. So the translation may not reflect the original precisely.
2.**** shows the word which can not be translated.
3.In the drawings, any words are not translated.

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention] This invention relates to the electrodes or film-electrode complex which are used for a fuel cell or various electrochemistry equipments, and those manufacture approaches.
[0002]
[Description of the Prior Art] A fuel cell is the low power plant of the burden to an environment at low excretions and high energy effectiveness. For this reason, it is in the limelight again in the rise to earth environmental protection in recent years. Compared with the conventional large-scale generation-of-electrical-energy facility, it is the power plant expected also in the future as power plants of a mobile, such as a comparatively small-scale distributed generation-of-electrical-energy facility, an automobile, and a vessel.
[0003] There is a class of a solid-state macromolecule mold, a phosphoric-acid mold, a solid acid ghost mold, a melting carbonate mold, alkali mold, etc. of fuel cells according to the class of electrolyte used. Especially, compared with other fuel cells, warm-up time of an operating temperature is short at low temperature, and a polymer electrolyte fuel cell has the descriptions which high power tends to acquire, like that it can count upon small lightweight-ization, and it is strong to vibration, and fits the power source of supply of a mobile.
[0004] The fuel cell is constituted considering the cel into which the electrolyte used as the anode with which the reaction which bears a generation of electrical energy occurs, the electrode of a cathode, and an anode and the ion conductor between cathodes was inserted with the separator between each as a unit. The electrode consists of promotion of gaseous diffusion, an electrode substrate (it is also called a charge collector) which performs ** (**) **, and an electrode catalyst bed which actually serves as an electrochemical reaction place. For example, in the anode electrode of a polymer electrolyte fuel cell, fuel gas reacts on a catalyst front face, a proton and an electron are produced, an electron is conducted to an electrode substrate, and a proton is conducted to the electrolytic proton exchange film. For this reason, it is required for an anode electrode that gaseous diffusion nature, electronic conductivity, and ionic conduction nature should be good. On the other hand, in a cathode electrode, the proton which oxidation gas has conducted from the electrolyte on the catalyst bed front face, and the electron conducted from the electrode substrate react, and water is generated. For this reason, it is also necessary to discharge efficiently the water generated with gaseous diffusion nature, electronic conductivity, and ionic conduction nature.
[0005] From such a point, in the electrode substrate (charge collector), it had conductivity, and the good porosity electric conduction sheet of gas permeability has been used. For example, the thing of JP,6-20710,A, JP,7-326362,A, or JP,7-220735,A is proposed. The charge collector indicated by these consists of a porous carbon plate to which it comes to bind the carbon fiber of short die length with carbon.
[0006]
[Problem(s) to be Solved by the Invention] Although the above-mentioned porosity electric conduction sheet of gas permeability was good, when coating of the electrode catalyst bed was carried out on the sheet, the catalyst coating liquid into a hole permeated and the lump phenomenon was seen. The catalyst which is not used effectively will increase according to this catalyst **** lump phenomenon. Since the catalyst of noble metals is used in a fuel cell, that the catalyst which is not used effectively increases leads to the cost rise of an electrode. Especially a polymer electrolyte fuel cell has the high expectation for an automotive application. Cost also serves as an important factor with the engine performance at adaptation in an automotive application. If low cost-ization is made, as for the current polymer electrolyte fuel cell, much more spread is expected. For this reason, the electrode with few catalyst **** lumps was called for.

[0007] By solving the above-mentioned technical problem and obtaining an electrode with few catalyst **** lumps, the use effectiveness of this invention of a catalyst improves and it aims at the low cost-ized electrode by the amount reduction of catalysts being obtained.
[Means for Solving the Problem] In this invention, in order to solve the above-mentioned technical problem, it has the following configuration.
[0008] That is, in the electrode which consists of an electrode substrate and an electrode catalyst bed at least, the electrode of this invention is characterized by the thickness of this mixolimnion being 20 micrometers or less while this electrode catalyst bed permeates and it forms the mixolimnion into this electrode substrate.
[0009] Moreover, although the manufacture approach of the electrode of this invention is manufactured by preparing an electrode catalyst bed on an electrode substrate, it is characterized by applying electrode catalyst coating liquid on this electrode substrate, and preparing this electrode catalyst bed.
[0010] Furthermore, the electrode of this invention is applied to film-electrode complex (MEA), and also is applied also to usual electrochemistry equipment, especially a polymer electrolyte fuel cell, and is applied also to the mobile and automobile using this fuel cell.
[0011]
[Embodiment of the Invention] Hereafter, the gestalt of desirable operation of this invention is explained.
[0012] This invention is characterized by the thickness of the mixolimnion to which this electrode catalyst bed permeates into this electrode substrate being 20 micrometers or less in the electrode which consists of an electrode substrate and an electrode catalyst bed at least, and neither the electrode substrate used here nor especially an electrode catalyst bed is limited.
[0013] Since the mixolimnion in this invention is a layer to which an electrode catalyst bed permeates into an electrode substrate, the layer (henceforth a pure electrode catalyst bed) constituted by only the constituents (for example, polymer containing a catalyst metal, a catalyst particle, carbon black, and a fluorine atom etc.) of the electrode catalyst bed which does not contain an electrode substrate is not contained in said mixolimnion. Therefore, it is calculated by the thickness of a pure electrode catalyst bed not being included in the thickness of the mixolimnion of this invention, and excepting it. However, in the electrode of this invention, it does not bar also having said pure electrode catalyst bed. Therefore, a pure electrode catalyst bed may also be contained in the electrode catalyst bed of this invention with a mixolimnion.
[0014] In this invention, if there are few electrode substrates that an electrode catalyst bed permeates into an electrode substrate, in some of layers or fields, the condition that the component of an electrode catalyst exists in the opening part in which the component of an electrode substrate does not exist is meant. The manufacture approach that the electrode catalyst component of the liquid condition which is not solidified or fixed to the electrode substrate already formed to be sure is formed by ******** is one of the suitable manufacturing methods of the mixolimnion of this invention, or an electrode catalyst bed. However, the mixolimnion or electrode catalyst bed of this invention does not necessarily mean limiting, if formed by this manufacture approach.
[0015] It cannot be overemphasized that the thickness of the mixolimnion in this invention is average thickness, therefore it is technical within the limits of this invention as long as it is filling with the average, even if there is a part with which the numerical range of this invention is not filled locally. 15 micrometers or less of thickness of said mixolimnion are 10 micrometers or less still more preferably preferably. In addition, although not limited especially, it is desirable that it is 3 micrometers or more, and it is more desirable that it is 5 micrometers or more. When less [when it exceeds said upper limit, the amount of catalysts for which many permeate lumps are used effectively will fall, and / than said lower limit] and film-electrode complex is created, resistance may become large and it is because it is not desirable.
[0016] In this invention, the thickness of the mixolimnion to which an electrode catalyst bed permeates into an electrode substrate can be checked by scanning electron microscope (SEM) observation of an electrode cross section. Generally, an electrode substrate is a vesicular structure, and since an electrode catalyst bed is the structure filled up with the particle, the mixolimnion which the electrode catalyst particle to the inside of a porous electrode substrate permeated is observed. Moreover, the mixolimnion to which an electrode catalyst bed permeates an electrode substrate may be unable to observe clearly like [in case an electrode substrate contains conductive particles, such as carbon powder,]. In such a case, asking for the thickness of a mixolimnion is possible by observing whether the precious metal catalyst of the platinum contained in an electrode catalyst permeates by the electrode substrate throat top by using together SEM and X-ray microanalysis (XMA) (SEM-XMA). It is possible to ask for the thickness of a mixolimnion by various technique, without being especially limited besides above-mentioned SEM or above-mentioned SEM-XMA.

[0017] In SEM-XMA, a pure electrode catalyst bed and a mixolimnion are measured in the following procedures. First, the interface of a conductive liner sheet and a pure electrode catalyst bed is checked from SEM observation, and the thickness of a pure electrode catalyst bed is measured. Next, existence of Pt used for an electrode catalyst by XMA measurement is checked by the shade of a screen, and the thickness of the sum total of a pure electrode catalyst bed and the mixolimnion which permeated the conductive liner sheet is measured. It becomes possible from both difference to ask for the thickness of a mixolimnion.
[0018] Although electric resistance is low and it is possible to use without being limited especially if ** (**) ** can be performed as an electrode substrate used for this invention, the description of this invention is discovered especially in a porosity electric conduction sheet. As a component of an electrode substrate, that which is mainly concerned with conductive mineral matter is mentioned, for example, and carbon material, such as a baking object from a polyacrylonitrile, a baking object from a pitch, a graphite, and expanded graphite, stainless steel, molybdenum, titanium, etc. are illustrated as this conductive mineral matter. the case where especially the gestalt of conductive mineral matter is used for the electrochemistry equipment which uses a gas for an electrode active material like a fuel cell although the shape of fibrous or a particle etc. is not limited -- the fibrous conductivity mineral matter (inorganic conductivity fiber) from the point of gas permeability -- especially a carbon fiber is desirable. as the porosity electric conduction sheet using inorganic conductivity fiber -- textile fabrics or a nonwoven fabric -- any structure is usable. For example, the carbon cross made from the carbon paper TGP series by Toray Industries, Inc., SO series, and E-TEK etc. is used.
[0019] That whose thickness when applying the uniform planar pressure of 2.9MPa(s) in the thickness direction is 0.02-0.3mm as an electrode substrate used for this invention is desirable. It is 0.04-0.2mm more preferably. When thinner than 0.02mm, in case it uses for a fuel cell, an electrode substrate is buried in the gas passageway of a separator, the diffusion and permeability to the direction of a field become low, and reinforcement becomes it is weak and lacking in workability. When thicker than 0.3mm, the electric resistance of the thickness direction increases. In addition, thickness sandwiches an electrode substrate by the vitrified charcoal blank of two sheets which has a smooth front face by uniform thickness, and pressurizes it by the uniform planar pressure of 2.9MPa, and it asks for it from the difference of spacing of an up-and-down indenter [time / of inserting with the time of not inserting an electrode substrate]. In measurement of spacing of an indenter, spacing of an indenter is measured with minute displacement detection equipment at the both ends which face across the central point of an indenter, and spacing of an indenter is computed as the average of spacing of both ends. In order to consider as uniform planar pressure, one indenter makes adjustable the include angle which receives in a round support and the pressurization side of an up-and-down indenter makes.
[0020] The thickness measured by the planar pressure of 13kPa of the electrode substrate which serves as the above-mentioned thickness when the uniform planar pressure of 2.9MPa(s) is applied in the thickness direction has 0.1-2.0 desirablemm, and its 0.2-1.2mm is more desirable. If it exceeds 2mm, an electrode substrate becomes bulky, an electrode substrate will be suitable in the thickness direction, or the reinforcement of electrode equipments will become weak. In order to make it the thickness of less than 0.1mm, the need of binding an electrode substrate firmly by a lot of high polymers comes out.
[0021] It is desirable that it is 10 - 220 g/m2 as eyes of an electrode substrate. It is 20 - 120 g/m2 more preferably. In less than two 10 g/m, the reinforcement of an electrode substrate becomes low. Moreover, when it constructs on the polyelectrolyte film, a catalyst bed, and the time of unification of an electrode substrate and a cell, an electrode substrate becomes thin and the diffusion / transparency effectiveness to the direction of a field becomes inadequate. When 220 g/m2 was exceeded and it constructs on a cell, an electrode substrate becomes thick and resistance becomes large.
[0022] When the uniform planar pressure of 2.9MPa(s) is applied in the thickness direction, as for the consistency of an electrode substrate, it is desirable that it is 0.3 - 0.8 g/cm3. 0.35 - 0.7 g/cm3 is more desirable, and 0.4 - 0.6 g/cm3 is still more desirable. It asks for the consistency of the electrode substrate when applying the uniform planar pressure of 2.9MPa(s) in the thickness direction by count from the thickness of the electrode substrate when applying the uniform planar pressure of 2.9MPa(s) in the eyes and the thickness direction of an electrode substrate. In order for an electrode substrate to make diffusion and permeability high, it is necessary to make porosity high but, and if the consistency when applying the uniform planar pressure of 2.9MPa(s) in the thickness direction becomes larger than 0.8 g/cm3, porosity will fall and diffusion and permeability will become inadequate. Moreover, if smaller than 0.3 g/cm3, the resistance of the thickness direction will become large.

[0023] As for an electrode substrate, it is desirable that the pressure loss at the time of making 14cm [/second] air penetrate in the thickness direction in the condition of not performing pressurization by the planar pressure to the thickness direction is below 98Pa (10mmAq) in respect of the gaseous diffusion nature of an electrode substrate. Below 29Pa (3mmAq) is more desirable, and below 9.8Pa (1mmAq) is still more desirable.
[0024] More than the 0.49N/10mm width of face of the tensile strength of an electrode substrate is desirable, more than its 1.96N/10mm width of face is more desirable, and more than its 4.9N/10mm width of face is still more desirable. When tensile strength is low, there is a problem that possibility that a sheet will be damaged increases, in high order processing of electrode equipments.
[0025] In case an electrode substrate is used as the time of unification of the polyelectrolyte film, a catalyst bed, and an electrode substrate, or a cell, it is pressurized in the thickness direction and may break. Moreover, since it is pressurized in the thickness direction where a fluting separator is faced when using it as a cell, in addition to a big pressure being applied to the part which faces the crest of a fluting separator, the part which faces a crest and the boundary of a trough tends to break. When an electrode substrate breaks, omission of the broken inorganic conductivity matter, the fall of an electrode substrate on the strength, electric resistance increase of the direction of a field, etc. may take place, and the electrode engine performance may fall.
[0026] It is desirable that the weight percentage reduction after an electrode substrate's applying the uniform planar pressure of 2.9MPa(s) in the thickness direction for 2 minutes and canceling the planar pressure of the above-mentioned thing is 3% or less. It is because there is a problem of the electrode substrate with weight percentage reduction higher than 3% being weak after planar pressure discharge, and being easy to break in handling. Thereby, it is hard to break at the time of pressurization, and can prevent that it becomes impossible to use a fuel cell by destruction of an electrode substrate. It is 1% or less still more preferably 2% or less preferably.
[0027] In addition, measurement of weight percentage reduction is performed by [as being the following]. First, an electrode substrate is cut into a round shape with a diameter of 46mm, and weight is measured. Next, it is larger than the electrode substrate, and the electrode substrate cut by the vitrified charcoal blank of two sheets which has a smooth front face is inserted, it pressurizes so that it may become the pressure of 2.9MPa(s) per area of an electrode substrate, and it maintains for 2 minutes. A pressure is removed, an electrode substrate is taken out, the direction of a field is turned perpendicularly, and it is made to fall from height of 30mm. After performing this fall 10 times, weight is measured, and weight percentage reduction is computed.
[0028] Measurement of the electric resistance R of an electrode substrate is based on a degree. Two test electrode plates with which copper foil with width of face of 50mm, a die length [of 200mm], and a thickness of 0.1mm was stuck on one side of the vitrified charcoal blank which has the flat surface where a front face with width of face of 50mm, a die length [of 200mm], and a thickness of 1.5mm is smooth are prepared. Two test electrode plates keep uniform spacing substantial, and it is made for the fields of a vitrified charcoal blank to be countered and located in them. The terminal for currents is prepared in each end of two test electrode plates, and the terminal for electrical potential differences is prepared in each other end. The sheet with a diameter of 46mm cut down circularly is inserted in said gap, and is laid in the center section of two test electrode plates. A test electrode plate is moved so that the pressure of 0.98MPa(s) may act on the laid sheet. With the terminal for currents, the current of 1A is passed between two test electrode plates. With the terminal for electrical potential differences, electrical-potential-difference [at this time] V (V) is measured. The value of the measured electrical potential difference V is used, and Resistance R (momega and cm2) is called for by the degree type.
R=Vx2.3x2.3xpix1000 -- here, pi is a circular constant.
[0029] It is desirable that it is two or less 100m ohm-cm, as for the electric resistance of a porosity conductive liner sheet, it is more desirable that it is two or less 50m ohm-cm, and it is still more desirable that it is two or less 15m ohm-cm. It is desirable that it is two or less 150m ohm-cm, as for the electric resistance of the electrode substrate which contains a water-repellent fluororesin like the after-mentioned, it is more desirable that it is two or less 70m ohm-cm, and it is still more desirable that it is two or less 30m ohm-cm.
[0030] the electrode substrate of the above [electrode substrate] -- in addition, the porosity electric conduction sheet the die length of inorganic conductivity fiber is at least 3mm, and is [sheet] at least 5 times the thickness of a sheet can also be used including the paper-like sheet which comes to bind with a high polymer the inorganic conductivity fiber by which orientation was substantially carried out in the

random direction into the 2-dimensional flat surface. Here, the thickness of a sheet is JIS. It measures according to P8118. Planar pressure at the time of measurement is taken as 13kPa(s). The semantics of saying [that orientation of the inorganic conductivity fiber is substantially carried out into a 2-dimensional flat surface] means that it lies so that inorganic conductivity fiber may form one field in general. The short circuit with a counter electrode and the breakage of inorganic conductivity fiber by inorganic conductivity fiber can be prevented by this.

[0031] Although the die length of inorganic conductivity fiber is at least 3mm or more in order to make the reinforcement and handling nature of an electrode substrate high and to carry out orientation of the inorganic conductivity fiber into a 2-dimensional flat surface substantially, 6mm or more costs 4.5mm or more still more preferably preferably. In less than 3mm, it becomes difficult to maintain reinforcement and handling nature. Moreover, in order to make the orientation of the inorganic conductivity fiber carry out in the random direction into a 2-dimensional flat surface substantially, the die length of inorganic conductivity fiber is preferably made into 12 or more times still more preferably 8 or more times 5 or more-time thick Mino of an electrode substrate. In less than 5 times, reservation of two-dimension orientation becomes difficult. In order to make the orientation of the upper limit of the die length of inorganic conductivity fiber carry out in the random direction into a 2-dimensional flat surface substantially, its 30mm or less is desirable, and it is more desirable, and is still more desirable. [of 8mm or less] [of 15mm or less] If inorganic conductivity fiber is too long, it will be easy to generate a maldistribution, and while much fiber has been bundles-like, it may remain. In that case, a bundle-like part has low voidage, since the thickness at the time of pressurization becomes thick, a high pressure is applied at the time of pressurization, and problems, such as destruction of an electrode substrate, polyelectrolyte film, and local lamination of an electrode catalyst bed, become easy to arise.

[0032] Moreover, as for the gestalt of inorganic conductivity fiber, it is desirable that it is a straight line-like so that a short circuit with the counter electrode by fiber can be prevented more completely. Here, when die-length L (mm) which exists in the die-length direction of fiber where the external force which bends inorganic conductivity fiber is removed is taken, inorganic straight-line-like conductivity fiber measures gap [from linearity] delta (mm) to die-length L, and means that whose delta/L is 0.1 or less in general. On the other hand, when making the orientation of the nonlinear-like fiber carry out in the random direction into a 2-dimensional flat surface substantially, it has the fault of being easy to turn to the direction of three dimensions.

[0033] In creation of an electrode substrate, there are a wet method which is made to distribute inorganic conductivity fiber and mills paper in the medium of a liquid, and dry process which is made to distribute inorganic conductivity fiber and is made to lie in air as an approach of making the orientation of the inorganic conductivity fiber carrying out in the random direction into a 2-dimensional flat surface substantially. In order to carry out orientation of the inorganic conductivity fiber into a 2-dimensional flat surface substantially certainly, and in order to make reinforcement of inorganic conductivity fiber high, a wet method, especially the so-called paper-making method are desirable.

[0034] In order to prevent breakage of the inorganic conductivity matter at the time of pressurization and to make weight percentage reduction of an electrode substrate into 3% or less as mentioned above in an electrode substrate, its carbon staple fiber which cut the carbon fiber is desirable, as for the fiber to be used, what applied tension at the time of heat treatment is more desirable, and what was extended at the time of heat treatment is still more desirable.

[0035] As a carbon fiber, a polyacrylonitrile (PAN) system carbon fiber, a phenol system carbon fiber, a pitch based carbon fiber, a rayon system carbon fiber, etc. are illustrated. Especially, a PAN system carbon fiber is desirable. As for a PAN system carbon fiber, compared with a pitch based carbon fiber, whenever [compressive-strength and **** breaking extension] is large, and it cannot break easily. This is considered to be based on the difference of crystallization of the carbon which constitutes a carbon fiber. In order to obtain the carbon fiber into which it is hard to break, the heat treatment temperature of a carbon fiber has desirable 2,500 degrees C or less, and its 2,000 degrees C or less are more desirable.

[0036] The carbon staple fiber used into the electrode substrate of this invention is good for a diameter D (micrometer), tensile strength sigma (MPa), and relation with a modulus of elasticity in tension E (MPa) to have satisfied the degree type. The electrode substrate which consists of such a carbon staple fiber is for being hard to break. Namely, the diameter of a carbon staple fiber is thin, tensile strength is strong, as for a carbon staple fiber, the one where a modulus of elasticity in tension is lower cannot break easily, and an electrode substrate stops being able to break easily at the time of pressurization.

sigma/(ExD) >=0.5x10-3 -- here -- the tensile strength of a carbon fiber, and a modulus of elasticity in

tension -- JIS It measures according to R7601. In the case of the flat carbon fiber of a cross section, let the average (a+b) (/2) of a major axis (a) and a minor axis (b) be a diameter. When the carbon staple fiber with which classes differ is mixed, the value which carried out the weighted mean about D, sigma, and E, respectively is used. It is sigma/(ExD) >=1.1x10-3 preferably, and is sigma/(ExD) >=2.4x10-3 more preferably.

[0037] Whenever [**** breaking extension / of a carbon staple fiber] is 1.2% or more preferably [that it is 0.7% or more] because of the reinforcement of an electrode substrate, and more preferably, and is 1.8% or more still more preferably. Whenever [**** breaking extension] is the value which **(ed) tensile strength (sigma) by the modulus of elasticity in tension (E).

[0038] Moreover, since breakage of a carbon staple fiber is generated in various situations, it is desirable that they are 500 or more MPas, as for the tensile strength of a carbon staple fiber, it is more desirable that they are 1,000 or more MPas, and it is still more desirable [tensile strength] that they are 2,000 or more MPas.

[0039] As for the diameter of the inorganic conductivity fiber used for an electrode substrate, it is desirable that it is 20 micrometers or less. 12 micrometers or less are more desirable and 8 micrometers or less are still more desirable. On the surface of an electrode substrate, an opening 5 to 10 times the diameter of the diameter of inorganic conductivity fiber is observed. This opening will become large if the diameter of fiber becomes thick. The conductive interlayer of this invention controls that the electrode engine performance falls, when an electrode catalyst bed permeates this opening. Since it will be necessary to thicken a conductive interlayer and will check gas permeability and eccritic [of water] if this opening is too large, the thinner one of the diameter of fiber is desirable. Moreover, inorganic conductivity fiber cannot break easily at the time of the pressurization of the thickness direction, so that it is thin. On the other hand, if the diameter of inorganic conductivity fiber becomes thin too much, since permeation to the electrode substrate of a catalyst bed will stop being able to happen easily at the time of unification, as for the diameter of fiber, it is desirable that it is 2 micrometers or more. When the fiber from which a diameter differs is mixed, it asks for a diameter with a weighted mean.

[0040] Below 200micro ohm-m of the volume resistivity of the inorganic conductivity fiber used for an electrode substrate is desirable because of the reduction in resistance of an electrode substrate, below its 50micro ohm-m is more desirable, and below its 15micro ohm-m is still more desirable. Measurement of the volume resistivity of inorganic conductivity fiber is JIS. It carries out according to R7601. When the fiber length defined by said measurement formula is not obtained, it measures by the obtained fiber length.

[0041] When using a carbon fiber for an electrode substrate, that whose atomic ratio (an oxygen atomic number / carbon atomic number) of the surface oxygen atom and carbon atom by the X-ray-photoelectron-spectroscopy analysis method is 0.10 or less still more preferably 0.20 or less preferably 0.35 or less is good. When obtaining an electrode substrate by the wet paper-making method, and the atomic ratio of an oxygen atom and a carbon atom is high, it is for distribution of a carbon staple fiber to become difficult and for a maldistribution to increase. If 0.35 is exceeded, it will become difficult to obtain a uniform electrode substrate. In order to make low the atomic ratio of an oxygen atom and a carbon atom, the surface preparation of a carbon fiber and grant of a sizing agent are stopped, or there is the approach of removing a surface oxygen atom by heat treatment in inactive or reducing atmosphere.

[0042] An electrode substrate is an embodiment also with desirable also performing partial hydrofuge ** hydrophilic processing for forming the exhaust passage of a water-repellent finish which prevents the gaseous diffusion and the penetrable fall by stagnation of water and which is performed for accumulating, and water, addition of carbonaceous powder performed in order to lower resistance.

[0043] The electrode substrate of this invention is an embodiment also with desirable a conductive particle, especially a conductive inorganic particle also being included from points, such as thickness fall control at the time of compression, improvement in a consistency, and reduction of electric resistance, when using the porosity electric conduction sheet which consists of a conductive inorganic fiber as mentioned above. As such a conductive inorganic particle, the carbon material from electric resistance or a corrosion resistance point, especially a carbon particle are desirable.

[0044] It is also desirable to use for an electrode substrate the porosity electric conduction sheet with which it comes to arrange the conductive inorganic particle which has flexibility especially in the shape of a sheet. Thereby, there are few omission of a constituent, or even if mechanical force acts, it is hard to break, and the purpose of electric resistance of offering a cheap electrode substrate low becomes possible. The above-mentioned purpose can be attained by using an expanded graphite particle as a conductive inorganic particle which has flexibility especially.

[0045] Here, an expanded graphite particle means the graphite particle which a graphite particle is made to expand by heating quickly after being intercalation-compound-ized with a sulfuric acid, a nitric acid, etc., and is obtained. Usually, the distance between layers in the crystal structure of an expanded graphite particle is that [about 50 to 500 times] of a raw material graphite particle.
[0046] An expanded graphite particle is rich in the deformans of a configuration in itself. This property is expressed by the language called flexibility. This flexibility is observed by the gestalt-compatibility of the expanded graphite particle to other bodies which adjoin an expanded graphite particle and it. If expanded graphite particles receive a pressurization operation after at least parts have overlapped, according to a pressurization condition, this gestalt-compatibility will deform mutually, and when particles join partially at least, it will be observed. Moreover, the nominal member used when they are made to arrange this gestalt-compatibility in the shape of a sheet in an expanded graphite particle and the condition that permeability is secured for example, the conductive inorganic particle which does not have the flexibility used conventionally [, such as carbon black,] -- Or when the inorganic conductivity fiber used conventionally [, such as a carbon fiber,] is both pressurized, in accordance with the shape of an appearance of a nominal member, an expanded graphite particle is transformed and is observed by being joined to this nominal member.
[0047] Although the electrode substrate of this invention is an embodiment also with desirable other conductive particles and conductive fiber also being included in addition to the conductive particle which has flexibility, the electrode substrate the both sides of this conductive fiber and a conductive particle excelled [electrode substrate] in thermal resistance, oxidation resistance, and elution-proof nature by consisting of an inorganic material is obtained. As a conductive inorganic particle which does not have flexibility, although carbon black powder, graphite powder, metal powder, ceramic powder, etc. may also be included, the carbon material of carbon black, graphite, or carbonaceous is preferably mentioned from the point of electronic conductivity and corrosion resistance, for example. As such carbon material, carbon black, such as oil furnace black, channel black, lamp black, thermal black, and acetylene black, is desirable from the magnitude of electronic conductivity and specific surface area. as oil furnace black -- the Cabot Corp. make -- Balkan Peninsula XC-72, the Balkan Peninsula P, black PARUZU 880, black PARUZU 1100, black PARUZU 1300, black PARUZU 2000, and legal one -- the KETCHIEN black EC by 400 and LION, and the Mitsubishi Chemical make -- #3150, #3250, etc. mention -- having -- as acetylene black -- DIN by DENKI KAGAKU KOGYO K.K. -- a turnip -- a rack etc. is mentioned. Moreover, there are an artificial graphite, carbon, etc. which are obtained from organic compounds, such as a natural graphite besides carbon black, a pitch, corks, a polyacrylonitrile, phenol resin, and furan resin. Moreover, it is possible to also use the carbon material which carried out after-treatment processing of these carbon material. the inside of such carbon material -- especially Balkan Peninsula XC-72 by Cabot Corp., and DIN by DENKI KAGAKU KOGYO K.K. -- a turnip -- a rack, the LION KETCHIEN black, etc. are preferably used from the point of electronic conductivity.
[0048] In addition, although it should be suitably decided as an addition of the conductive particle to an electrode substrate according to the specific surface area of the electrode characteristic demanded or the matter used, electronic resistance, etc., 1 - 80% is desirable as a weight ratio in an electrode substrate, and 20 - 60% is still more desirable. When there are few electronic conductors, electronic resistance becomes low, and when many, all reduce the electrode engine performance, such as checking gas permeability.
[0049] The electrode substrate of this invention can also add a high polymer besides the above-mentioned conductive particle. This becomes strong to compression or tension, reinforcement and handling nature are raised, and the inorganic conductivity matter can separate from an electrode substrate, or can prevent turning to the thickness direction of an electrode substrate. In case the electrode substrate which carries out paper making of the inorganic conductivity staple fiber, and consists of a porosity electric conduction sheet especially is created, it is indispensable to use a high polymer as a binder. There are an approach of mixing fibrous and a granular and liquefied high polymer as an approach of making a high polymer binding, when making the orientation of the inorganic conductivity matter carry out in the random direction into a 2-dimensional flat surface substantially, an approach to which a high polymer fibrous to the aggregate with which orientation of the inorganic conductivity matter was substantially carried out in the random direction into the 2-dimensional flat surface, and liquefied is made to adhere. What the particle of a high polymer can distribute in liquids, such as an emulsion, dispersion, and a latex, and can be substantially dealt with as a liquid is contained in a liquefied concept. In order to strengthen binding of the inorganic conductivity matter or to make the electric resistance of an electrode substrate low, as for the polymeric material which binds the inorganic conductivity matter, it is desirable that they are fibrous, an emulsion, dispersion, and a latex. In

order to make content low in the case of a fibrous high polymer, it is desirable to use filament yarn.
[0050] As a high polymer which binds the inorganic conductivity matter The polymeric material which has carbon or silicon in a principal chain is desirable. For example, polyvinyl alcohol (PVA), Polyvinyl acetate (vinyl acetate), polyethylene terephthalate (PET), Polypropylene (PP), polyethylene, polystyrene, a polyvinyl chloride, Thermoplastics, such as a polyvinylidene chloride, acrylic resin, and polyurethane, Phenol resin, an epoxy resin, melamine resin, a urea-resin, alkyd resin, Others [thermosetting resin /, such as an unsaturated polyester resin, acrylic resin, and polyurethane resin,], Elastomers, such as thermoplastic elastomer, Butadiene Styrene (SBR), and Butadiene Acrylonitrile (NBR), rubber, a cellulose, pulp, etc. can be used. Water-repellent treatment of an electrode substrate may be performed to binding of the inorganic conductivity matter and coincidence using water-repellent resin, such as a fluororesin.
[0051] In order to make it hard to break an electrode substrate at the time of pressurization, since it will decrease that the high polymer's which binds the inorganic conductivity matter an electrode substrate breaks at the time of pressurization if the softer one is good, and soft high polymers, such as thermoplastics, an elastomer, rubber, a cellulose, and pulp, are used for a high polymer in using a high polymer with a fibrous or granular gestalt, it is desirable. Moreover, when using a high polymer with a liquefied gestalt, the thermosetting resin of a high polymer which denaturalized with elasticity ingredients, such as thermoplastics, an elastomer, rubber, and thermoplastics, an elastomer, rubber, is desirable, and an electrode substrate cannot break easily due to the aforementioned thermoplastics, an elastomer, and rubber at the time of pressurization, and it is more desirable.
[0052] It is desirable that the compressibility in 23 degrees C is 4,000 or less MPas, as for a high polymer, it is more desirable that they are 2,000 or less MPas, and it is still more desirable that they are 1,000 or less MPas. The high polymer with low compressibility is for making it hard to ease the stress concerning the binding section, to ease the stress which makes binding hard to separate and is applied to the inorganic conductivity matter, and to break.
[0053] In a cathode (an air pole, oxygen pole), the water as an electrode reaction product and the water which permeated the electrolyte generate a polymer electrolyte fuel cell. Moreover, in an anode (fuel electrode), a fuel is humidified and supplied for desiccation prevention of the polyelectrolyte film. Since it becomes the hindrance at the time of dew condensation of these water and the swelling of the high polymer by stagnation and water supplying an electrode reaction object, the lower one of the water absorption of a high polymer is good. It is 7% or less more preferably 20% or less.
[0054] It is also a desirable embodiment that a water-repellent macromolecule is included in an electrode substrate from such a point. Since the polymer (fluororesin) which contains fluorine atoms, such as a polytetrafluoroethylene (PTFE) and tetrafluoroethylene-hexafluoropropylene copolymer (FEP) and a tetrafluoroethylene-perfluoroalkyl vinyl ether copolymer (PFA), especially has high water repellence, it is used preferably. When using an electrode substrate as ** (**) **** for fuel cells, a water-repellent finish is indispensable and the water-repellent macromolecule in that case also brings about the adhesion effectiveness between the conductive mineral matter which constitutes an electrode substrate. This is useful from the reinforcement of an electrode substrate, and the point of electric resistance. PTFE, FEP, and PFA have high water repellence and oxidation resistance for which a fuel cell charge collector is asked, and PTFE and PFA are still more desirable in order to bring about the effectiveness that electric resistance is low.
[0055] As for the content to the electrode substrate of the above high polymers, it is desirable that it is in 0.1 - 50% of the weight of the range. Although little way of the content of a high polymer is good in order to make the electric resistance of an electrode substrate low, at less than 0.1 % of the weight, the reinforcement which is equal to handling runs short, and omission of the inorganic conductivity matter also increase. On the contrary, if it exceeds 40 % of the weight, the problem that the electric resistance of an electrode substrate increases will arise. It is 10 - 30% of the weight of the range more preferably.
[0056] The high polymer added to the electrode substrate is an embodiment also with desirable also calcinating above 200 degrees C. The above-mentioned fluororesin used for a water-repellent finish is heating more than the melting point, and water repellence and its binding property improve. Moreover, in high polymers other than a fluororesin, binding capacity improves by baking, and also the fall of electric resistance and corrosion resistance improvement are found. Especially in high polymers other than a fluororesin, it may be lacking in oxidation resistance, and in case it uses as electrodes for electrochemistry equipments, such as a fuel cell, electrode performance degradation may be brought about while in use. For this reason, it is desirable to calcinate, before using it for electrode creation time as an electrode, using the high polymer matter as a binder.

[0057] Especially the electrode catalyst bed in the electrode of this invention can use a well-known thing, without being limited. With the electrode catalyst bed, the matter contributed to the electronic conduction which promotes electrode reaction still more preferably, or ionic conduction is also included including the catalyst required for electrode reaction, or the electrode active material. Moreover, when an electrode active material (matter oxidized or returned) is a gas, it is required to have the structure which the gas tends to penetrate, and the structure urged also to discharge of the quality of a product accompanying electrode reaction is required. When using the electrode of this invention for a fuel cell, for hydrogen or oxygen, and a catalyst, noble-metals particles, such as platinum, and an electronic conductor are [an electrode active material / proton exchange resin and the quality of a resultant of carbon black and an ion conductor] water. A catalyst, an electronic conductor, and an ion conductor contact mutually, and, as for an electrode catalyst bed, the structure where an active material and a resultant go in and out efficiently is searched for.
[0058] Although the catalyst included in an electrode catalyst bed can use a well-known catalyst and it is not especially limited when using the electrode of this invention for a fuel cell, precious metal catalysts, such as platinum, palladium, gold, a ruthenium, and iridium, are used preferably. Moreover, two or more sorts of elements, such as an alloy of these precious metal catalysts and mixture, may be contained.
[0059] Especially as an electronic conductor (electric conduction material) contained in an electrode catalyst bed, although not limited, the inorganic conductivity matter is preferably used from the point of electronic conduction nature and corrosion resistance. Especially, carbon black, the carbon material of graphite or carbonaceous or a metal, and semimetal are mentioned. As such carbon material, carbon black, such as oil furnace black, channel black, lamp black, thermal black, and acetylene black, is desirable from the magnitude of electronic conductivity and specific surface area. as oil furnace black -- the Cabot Corp. make -- Balkan Peninsula XC-72, the Balkan Peninsula P, black PARUZU 880, black PARUZU 1100, black PARUZU 1300, black PARUZU 2000, and legal one -- the KETCHIEN black EC by 400 and LION, and the Mitsubishi Chemical make -- #3150, #3250, etc. mention -- having -- as acetylene black -- DIN by DENKI KAGAKU KOGYO K.K. -- a turnip -- a rack etc. is mentioned. Moreover, there are an artificial graphite, carbon, etc. which are obtained from organic compounds, such as a natural graphite besides carbon black, a pitch, corks, a polyacrylonitrile, phenol resin, and furan resin. As a gestalt of these carbon material, it can use fibrous besides the shape of a particle. Moreover, it is possible to also use the carbon material which carried out after-treatment processing of these carbon material. Also in such carbon material, Balkan Peninsula XC-72 by Cabot Corp. are especially used preferably from the point of electronic conductivity.
[0060] Although it should be suitably decided as an addition of these electronic conductors according to the specific surface area of the electrode characteristic demanded or the matter used, electronic resistance, etc., 1 - 80% is desirable as a weight ratio in an electrode catalyst bed, and 20 - 60% is still more desirable. When there are few electronic conductors, electronic resistance becomes low, and when many, all reduce the electrode engine performance -- check gas permeability or a catalyst utilization factor falls.
[0061] As for an electronic conductor, distributing to a catalyst particle and homogeneity is desirable in respect of the electrode engine performance. For this reason, the catalyst particle and the electronic conductor are beforehand distributed well as coating liquid, and the approach of applying this coating liquid on the porosity electric conduction sheet which prepared the conductive interlayer is used preferably.
[0062] When using an electrode catalyst bed for a fuel cell, it is also a desirable embodiment to use the catalyst support carbon which the catalyst and the electronic conductor unified. By using this catalyst support carbon, the use effectiveness of a catalyst improves and it contributes to low cost-ization. When catalyst support carbon is used for an electrode catalyst bed, it is also possible to add an electric conduction agent further. Also as such an electric conduction agent, above-mentioned carbon black is used preferably.
[0063] It is possible to use without limiting especially a well-known thing as an ion conductor used for an electrode catalyst bed. As an ion conductor, although various organic and inorganic materials are well-known, when using for a fuel cell, the polymer which has ion exchange groups, such as a sulfonic group which improves proton conductivity, a carboxylic-acid radical, and a phosphoric-acid radical, is used preferably. The polymer which has the proton exchange group which consists of a fluoro alkyl ether side chain and a fluoro alkyl principal chain especially is used preferably. For example, Nafion made from DuPont, Aciplex by Asahi Chemical Co., Ltd., Flemion by Asahi Glass Co., Ltd., etc. are desirable. These ion-exchange polymers can be prepared into an electrode catalyst bed in the state of a solution or dispersion liquid. In this case, although especially the solvent that dissolves or decentralizes proton exchange resin is not limited, the soluble point of proton exchange resin to a polar solvent is desirable. You may be other polymers, such as a polymer, ethylene, styrene, etc. containing the above-mentioned fluorine atom which has a proton exchange group, these copolymers, and a blend.

[0064] In case an ion conductor creates an electrode catalyst bed, it is desirable from the point of the electrode engine performance to apply in the condition of having added beforehand to the coating liquid which uses an electrode catalyst particle and an electronic conductor as a main constituent, and having distributed to homogeneity, but after it applies an electrode catalyst bed, it may apply an ionic conductor. It is not limited [flow coat / a spray coat, brush coating, a DIP coat, a die coat, a curtain coat,] especially as an approach of applying an ionic conductor to an electrode catalyst bed.
[0065] Although it should not be suitably decided as an amount of the ion conductor contained in an electrode catalyst bed according to the electrode characteristic demanded, the electric conductivity of the ion conductor used, etc. and is not limited especially, 1 - 80% is desirable at a weight ratio, and 5 - 50% is still more desirable. When there are few ion conductors, ionic conductivity is low, when many, it is the point which checks gas permeability, and the electrode engine performance is all reduced.
[0066] The various matter other than the above-mentioned catalyst, an electronic conductor, and an ion conductor may be included in the electrode catalyst bed. In order to raise the binding property of the matter contained especially in an electrode catalyst bed, it is also a desirable embodiment that polymers other than above-mentioned proton exchange resin are included. although it is not what the polymer containing a fluorine atom is mentioned as such a polymer, and is limited especially -- a copolymer with the monomer of others for example, such as these copolymers, such as the Pori vinyl fluoride (PVF), polyvinylidene fluoride (PVDF), poly hexafluoropropylene (FEP), polytetrafluoroethylene, and polyperfluoro alkyl vinyl ether (PFA), or these monomeric units, ethylene, and styrene, -- a blend etc. can be used further. As a content in the catalyst bed of these polymers, 5 - 40% is desirable at a weight ratio. When there are too many polymer contents, an electron and ion resistance increase and the electrode engine performance falls.
[0067] An electrode catalyst bed is an embodiment also with desirable catalyst-polymer complex also having a three-dimensions mesh fine vesicular structure. Catalyst-polymer complex is polymer complex containing a catalyst particle, and it is the description that this complex has a three-dimensions mesh fine vesicular structure. In addition, "three-dimensions mesh fine porosity structure" means the condition of having the network structure of the shape of three dimensions with which catalyst-polymer complex was connected in three dimensions.
[0068] When the electrode catalyst bed has the three-dimensions mesh fine vesicular structure, it is desirable that the diameter of fine porosity is 0.05-5 micrometers. It is 0.1-1 micrometer more preferably. The diameter of fine porosity is a scanning electron microscope (SEM) etc., and from the photograph which photoed the front face, it can ask for it from the average of 100 or more pieces preferably 20 or more pieces, and it can usually be measured by 100 pieces. Since distribution of the diameter of fine porosity is large, as for the catalyst bed of the fine vesicular structure of this invention at the time of being manufactured by the wet coagulation method, it is desirable to take the average of as many apertures as possible.
[0069] As for the void content of a three-dimensions mesh fine vesicular structure, it is desirable that it is 10 - 95%. It is 50 - 90% more preferably. A void content is a percentage (%) which **(ed) what subtracted the volume which catalyst-polymer complex occupies from the whole catalyst bed product by the whole catalyst bed product. After applying a catalyst bed to an electrode substrate, the proton exchange film, and the other base material, it performs wet coagulation, but when it is difficult to ask a catalyst bed for a void content independently, after asking for the void content of an electrode substrate, the proton exchange film, and the other base material beforehand and asking for the void content containing these base materials and a catalyst bed, it is also possible to ask for a catalyst bed independent void content.
[0070] A void content is large and electronic conduction nature and its proton conductivity are [the thing of the three-dimensions mesh fine vesicular structure from which especially the electrode catalyst bed was obtained by the wet coagulation method has good discharge of gaseous diffusion nature or generation water, and] also good. Although catalyst particle diameter and the particle diameter of an addition polymer are increased or forming a hole using an ostomy agent etc. is performed in the conventional porosity-ization, the contact resistance between catalyst support carbon and between proton exchange resin will become large compared with an electrode catalyst bed by such porosity-ized method. Since the polymer complex which contained catalyst support carbon to it with the three-dimensions mesh fine vesicular structure by the wet coagulation method has become three-dimensions mesh-like, an electron and a proton tend to conduct this polymer complex, and discharge of gaseous diffusion nature or generation water also has good structure further for the fine vesicular structure.
[0071] When the electrode catalyst bed has the three-dimensions fine vesicular structure, the matter used for a catalyst, an electronic conductor, and an ion conductor can use the same matter as usual. However, in case the electrode catalyst bed which has a three-dimensions mesh fine vesicular structure is created, being based

on a wet coagulation method is desirable. Therefore, in the aforementioned case, it is desirable to use the polymer suitable for this wet coagulation method, and it is desirable although the polymer which distributes a catalyst particle well and does not deteriorate in the oxidation-reducing atmosphere in a fuel cell is used. although it is not what the polymer containing a fluorine atom is mentioned as such a polymer, and is limited especially -- a copolymer (for example, hexafluoropropylene-vinylidene fluoride copolymer) with the monomer of others for example, such as these copolymers, such as the Pori vinyl fluoride (PVF), polyvinylidene fluoride (PVDF), poly hexafluoropropylene (FEP), and polyperfluoro alkyl vinyl ether (PFA), or these monomeric units, ethylene, and styrene, -- a blend etc. can be used further.
[0072] It is an especially desirable polymer at the point that the catalyst-polymer complex which has a three-dimensions mesh fine vesicular structure by the wet coagulation method polyvinylidene fluoride (PVDF) and a hexafluoropropylene-vinylidene fluoride copolymer use a protonic polar solvent etc. as a coagulation solvent also in this using an aprotic polar solvent is obtained. as a solvent of these polymers, N-methyl pyrrolidone (NMP), dimethylformamide (DMF), dimethylacetamide (DMAC), propylene carbonate (PC), dimethyl imidazolidinone (DMI), etc. mention -- having -- as a coagulation solvent -- lower alcohol, such as water, and a methanol, ethanol, isopropanol, -- others -- the various organic solvents of ester, such as ethyl acetate and butyl acetate, an aromatic series system, or a halogen system are used.
[0073] In order to raise proton conductivity as a polymer of catalyst-polymer complex in addition to the above-mentioned polymer, the polymer which has a proton exchange group is also desirable. As a proton exchange group contained in such a polymer, especially although there are a sulfonic group, a carboxylic-acid radical, a phosphoric-acid radical, etc., it is not limited. Moreover, although the polymer which has such a proton exchange group is also chosen without being limited especially, the polymer which has the proton exchange group which consists of a fluoro alkyl ether side chain and a fluoro alkyl principal chain is used preferably. For example, Nafion made from DuPont etc. is desirable. Moreover, you may be other polymers, such as a polymer, ethylene, styrene, etc. containing the above-mentioned fluorine atom which has a proton exchange group, these copolymers, and a blend.
[0074] the polymer solution of Nafion could melt the commercial Nafion film to the aprotic polar solvent, and carried out the solvent permutation of the Nafion solution or this Nafion solution of a water-methanol-isopropanol mixed solvent made from Aldrich -- you may use. In this case, although the coagulation solvent in the case of wet coagulation should be suitably decided with the solvent of a Nafion solution, when the solvent of a Nafion solution is an aprotic polar solvent, as a coagulation solvent, water, various organic solvents besides alcohols and ester, etc. are desirable, and, in the case of a water-methanol-isopropanol mixed solvent etc., ester, such as butyl acetate, and various organic solvents are used preferably.
[0075] As for the polymer used for catalyst-polymer complex, copolymerization or blending and using are also desirable in the polymer containing the above-mentioned fluorine atom, or the polymer containing a proton exchange group. Especially the thing for which polymers, such as Nafion which has a fluoro alkyl ether side chain and a fluoro alkyl principal chain in a proton exchange group, are blended with polyvinylidene fluoride, the Pori (hexafluoropropylene-vinylidene fluoride) copolymer, etc. is desirable from the point of the electrode engine performance.
[0076] Although the main components of catalyst-polymer complex are catalyst support carbon and a polymer, and those ratios should not be suitably decided according to the electrode characteristic needed and it is not especially limited, 5 / 95 - 95/5 are preferably used by the weight ratio of catalyst support carbon / polymer. When using as an electrode catalyst bed for polymer electrolyte fuel cells especially, 40 / 60 - 85/15 are desirable by catalyst support carbon / polymer weight ratio.
[0077] It is also a desirable embodiment to add various additives to catalyst-polymer complex. For example, although there are electric conduction agents, such as carbon of the sake on an electronic conduction disposition, an additive which controls the polymer for the improvement in bending and the aperture of a three-dimensions mesh fine vesicular structure, it can use, without being limited especially. As an addition of these additives, 0.1 - 50% is desirable as a weight ratio to catalyst-polymer complex, and 1 - 20% is still more desirable.
[0078] As the manufacture approach of catalyst-polymer complex of having a three-dimensions mesh fine vesicular structure, what is depended on a wet coagulation method is desirable. After this wet coagulation method applies a catalyst-polymer solution constituent, this spreading layer is contacted to the coagulation solvent to a polymer, and coagulation deposit of a catalyst-polymer solution constituent and solvent extraction are performed to coincidence.
[0079] Catalyst support carbon distributes this catalyst-polymer solution constituent to homogeneity in a polymer solution. The thing of the above-mentioned [catalyst support carbon and a polymer] is used

preferably. About the solvent which melts a polymer, according to the polymer used, it should not be decided suitably, and is not limited especially. It is important for a polymer solution to distribute catalyst support carbon well. When a distributed condition is bad, in the case of wet coagulation, catalyst support carbon and a polymer cannot form complex and are not desirable.

[0080] Although the method of application according to viscosity, solid content, etc. of a catalyst-polymer solution constituent should be chosen and it should not be especially limited about the method of application, the general methods of application, such as a knife coating machine, a bar coating machine, a spray, a dip coater, a spin coater, a roll coater, a die coating machine, and a curtain coating machine, are used.

[0081] On the other hand, although not limited especially about the coagulation solvent to which wet coagulation of the polymer is carried out, either, the solvent which is easy to carry out the coagulation deposit of the polymer used, and has the solvent and compatibility of a polymer solution is desirable. Although not especially limited about the contact approach with the coagulation solvent with which wet coagulation is actually performed, especially carrying out a spray etc. is not a shower ring or the thing limited at a spreading layer about the coagulation solvent which is immersed in a coagulation solvent the whole base material and which contacts only a spreading layer on the oil level of a coagulation solvent.

[0082] Although it is possible spreading and to perform wet coagulation after that also in any of an electrode substrate or a solid electrolyte about the base material with which this catalyst-polymer solution constituent is applied, immediately after applying to an electrode substrate, it becomes possible to control a permeate lump of the catalyst bed to an electrode substrate by performing wet coagulation, and becomes the desirable embodiment of this invention. Moreover, after applying to an electrode substrate or base materials other than a solid electrolyte (imprint base material), performing wet coagulation after that and creating a three-dimensions mesh fine vesicular structure, an electrode substrate and a solid electrolyte may be made to imprint or pinch this catalyst bed. As an imprint base material in this case, the sheet of polytetrafluoroethylene (PTFE), a glass plate, a metal plate with which the fluorine and the silicone system carried out release agent processing of the front face, etc. are used.

[0083] When the electrode of this invention makes the mixolimnion to which an electrode catalyst bed permeates into an electrode substrate the thickness of 20 micrometers or less, especially the manufacture approach is not limited for the purpose of the useless thing which is not used effectively and which carry out catalyst reduction. Since electrode catalyst bed coating liquid is easy permeating an electrode substrate when using a porosity electric conduction sheet for an electrode substrate, the device not permeating is required in order to consider as the electrode of this invention. For example, there are approaches, such as enlarging the difference of the surface energy of the electrode substrate and the polymeric materials contained, and electrode catalyst bed coating liquid which make high viscosity of electrode catalyst bed coating liquid.

[0084] If viscosity of electrode catalyst bed coating liquid is made high, the permeate lump by the porosity electric conduction sheet will be controlled. In order to raise viscosity, the approach of adding various thickeners is in the catalyst bed coating liquid which makes high molecular weight of the high polymer contained in catalyst bed coating liquid which makes high solid content ratios other than the solvent of catalyst bed coating liquid. As an example of a thickener, although carbon black, such as high molecular compounds, such as celluloses, such as higher alcohol, such as polyhydric alcohol, such as a glycerol, and an octanol, a carboxymethyl cellulose, and hydroxypropylcellulose, polyvinyl alcohol, and a polyvinyl pyrrolidone, acetylene black, and KETCHIEN black, is desirable, it is not limited especially.

[0085] When using the surface energy difference of an electrode substrate, and the polymer and electrode catalyst bed coating liquid contained, it is that the static contact angle of an electrode substrate and electrode catalyst bed coating liquid considers as 50 degrees or more (preferably 70 degrees or more), and it is possible to control a permeate lump. When using for a fuel cell, in order that an electrode substrate may give a water-repellent finish, surface free energy is low including the fluororesin. For this reason, a static contact angle increases and permeates by using the electrode catalyst bed coating liquid containing the big solvent of surface free energy, and lump control is made. Proton exchange resin is contained in the electrode catalyst bed as an ion conductor. For this reason, in such a case, the catalyst bed coating liquid containing ion exchange resin contains water, it permeates because a static contact angle becomes large, and lump control is made. If N-methyl pyrrolidone besides water is used for the solvent of electrode catalyst bed coating liquid when a fluororesin is contained in an electrode substrate, a static contact angle will become large, and will permeate and lump control will be made. Measurement of a static contact angle is good by the general measuring method [say / a micro syringe dropping one drop of catalyst bed coating liquid on a base material, and measuring under a microscope from a side face].

[0086] The electrode of this invention is an embodiment also with desirable also considering as film-electrode complex (MEA:Membrane Electrode Assembly) by combining a solid electrolyte layer.
[0087] Especially if it is the solid electrolyte used for the usual fuel cell as a solid electrolyte which constitutes the solid electrolyte layer, it is not limited, but when the proton exchange film discovers the fuel cell engine performance of this invention, it is used preferably. It is not limited [radical / a sulfonic group, a carboxylic-acid radical, / phosphoric-acid] especially as a proton exchange group of the proton exchange film.
[0088] Although this proton exchange film should be suitably chosen according to the application and the environment where it is divided roughly into the perfluoro system of the copolymer which consists of a hydrocarbon system, and a fluorine atom content polymer especially a fluoro alkyl ether side chain and fluoro alkyl principal chains, such as a styrene-divinylbenzene copolymer which has the above-mentioned proton exchange group, especially a sulfonic group, and a fuel cell is used, a fluorine atom content polymer, especially its perfluoro system are desirable from the point of a fuel cell life. Moreover, the partial fluorine film which carried out the fluorine atom permutation partially is also used preferably. By the perfluoro film, Nafion made from DuPont, Asahi Chemical Aciplex, Asahi Glass Flemion, Japan Gore-Tex Goa-select, etc. are illustrated, and there are some which introduced the sulfonic group into the polymer and polyvinylidene fluoride of a trifluoro styrene sulfonic acid in the partial fluorine film. Moreover, the proton exchange film can use one sort of not only polymers but the bipolar membrane which stuck the copolymer of two or more sorts of polymers, and blend polymer and two or more sorts of film, the film which reinforced the proton exchange film with the nonwoven fabric, the porous film, etc.
[0089] It is not limited especially as the manufacture approach of film-electrode complex. Although an electrode catalyst bed is prepared on an electrode substrate, an electrode is generally created and this electrode is joined to solid electrolytes, such as proton exchange film, according to the property of an electrode catalyst bed or electrochemistry equipment, it should be suitably decided also about this junction condition.
[0090] When harnessing the property of the electrode of this invention, the manufacture approach of MEA by creating beforehand the electrode which consists of an electrode substrate and an electrode catalyst bed two sheets, arranging so that the electrode catalyst bed side of each electrode may meet the proton exchange film in the proton exchange film among these electrodes of two sheets, making this proton exchange film **** from said electrode of two sheets, and joining is desirable. this junction -- warming -- although it becomes a press, it is not limited especially about this condition, either. Generally, press temperature is 20 degrees C - 200 degrees C, and a press pressure is 1MPa-20MPa.
[0091] It is also the desirable manufacture approach to perform the process (process A) which prepares said electrode catalyst bed in front flesh-side both sides of the proton exchange film, and the process (process B) which prepares an electrode substrate in both the lateral surface of this electrode catalyst bed in this order as the other film-electrode complex manufacture approaches. This approach is an approach whose creation of MEA which consists of an electrode of this invention at the point which controls the catalyst bed **** lump by the base material is enabled in order not to perform catalyst bed spreading to an electrode substrate.
[0092] The MEA manufacture approach of carrying out coating of the electrode catalyst bed coating liquid on the proton exchange film, and preparing an electrode substrate after that especially is also desirable. In this case, since it is easy to swell the proton exchange film which applies catalyst coating liquid with water or an organic solvent, the solvent used for catalyst bed coating liquid needs to choose the solvent which cannot swell the proton exchange film easily. However, proton exchange resin will be contained in catalyst bed coating liquid, it will get down, and the proton exchange film will be swollen or melted in the solvent which dissolves this proton exchange resin. For this reason, in catalyst bed coating liquid, it is desirable to use the solvent distributed with gestalten, such as an emulsion, without dissolving the proton exchange resin contained. For example, it is not limited especially although the approach of solvent-removing the dispersion liquid of the approach of solvent-removing a proton exchange-resin solution, drying, grinding, and mixing and distributing the obtained proton exchange-resin powder and catalyst support carbon in the solvent which is not made to swell the proton-exchange film, or a proton exchange-resin solution and catalyst support carbon, drying, grinding, and re-distributing the obtained powder to proton exchange resin and the solvent do not swell etc. is mentioned.
[0093] Furthermore, in the above-mentioned process A, it is also the desirable MEA manufacture approach to apply electrode catalyst coating liquid on an electrode substrate or imprint base materials other than the proton exchange film, to form an electrode catalyst bed, and to imprint this on the proton exchange film. It is possible to use imprint base materials which consist of fluororesins, such as various kinds of resin, or PTFE,

PFA, FEP, such as a sheet and a film, a glass plate, etc. as an imprint base material in this case. It is possible to imprint on the proton exchange film by carrying out coating of the electrode catalyst bed to especially a sheet and a film, and carrying out the roll press of it to the proton exchange film.

[0094] Moreover, in the above-mentioned process B, it is also the desirable MEA manufacture approach to prepare an electrode substrate by carrying out coating of the matter which constitutes an electrode substrate to the proton exchange film. MEA is created in inorganic conductivity fiber and the particle which constitute an electrode substrate liquefied or by spraying the proton exchange film which prepared the electrode catalyst bed by the shape of a solid-state. When the inorganic conductivity matter which constitutes an electrode substrate especially is a carbon staple fiber, it is also desirable to carry out coating by creating beforehand the dispersion liquid containing this and a fluorine atom content polymer, and spraying these dispersion liquid on the proton exchange film which prepared the electrode catalyst bed.

[0095] The film-electrode complex (MEA) which consists of the electrode which consists of the electrode substrate and electrode catalyst bed of this invention or this electrode, and a solid-electrolyte membrane can be adapted for various electrochemistry equipments. Inside or a fuel cell, and a water electrolysis layer are desirable, and still more suitable for a polymer electrolyte fuel cell also in a fuel cell. Although there are what uses hydrogen as a fuel, and a thing which uses hydrocarbons, such as a methanol, as a fuel in a fuel cell, it can use without being limited especially.

[0096] Furthermore, although it thinks especially as an application of the fuel cell using the electrode catalyst bed of this invention, without being limited, in a polymer electrolyte fuel cell, the power source of supply of the mobile which is a useful application is desirable. It is a mobile with automobiles, such as a passenger car, a bus, and a truck, especially desirable a vessel, a railroad, etc.

[0097]

[Example] It explains further using an example per detail of this invention below.

[0098] Using carbon paper (Toray Industries TGP-H -060) as a creation porosity electric conduction sheet of an example 1 (1) electrode substrate, it sank into PTFE dispersion liquid (Daikin Industries make: Pori Flon TFE D-1, 0.2 to 0.4 micrometer dispersion mean particle diameter, 60 % of the weight, water solution), and this was calcinated at 370 degrees C after desiccation. PTFE was attached and the amount was 20 % of the weight.

[0099] (2) The Nafion solution made from Aldrich of preparation marketing of catalyst bed coating liquid (5 % of the weight) was condensed, and it could be 15 % of the weight. Catalyst support carbon (catalyst ;P. t, VulcanXCmade from carbon;Cabot- 72, amount of platinum support;50wt%) 3g was added to 10g of this concentration Nafion solution, and the catalyst bed coating liquid which stirs well and consists of a catalyst-polymer constituent was prepared.

[0100] (3) On the porosity electric conduction sheet created with spreading of electrode catalyst bed coating liquid, and the creation above (1) of the electrode by desiccation, the catalyst bed coating liquid prepared above (2) was applied, it dried, and the electrode which consists of an electrode substrate and an electrode catalyst bed was created. Amount 0.5 mg/cm2 with platinum and Nafion were attached, and the obtained electrode was amount 0.3 mg/cm2.

[0101] Distribution of platinum according the cross-section SEM photograph of this electrode to X-ray microanalysis is shown in drawing 1 (1) again at drawing 1 (3). The pure catalyst bed in which the thickness of the mixolimnion which the electrode catalyst bed permeated to the electrode substrate does not contain 10 micrometers and a mixolimnion was 15 micrometers.

[0102] Like the creation example 1 of the example 1 (1) electrode substrate of a comparison, using carbon paper (Toray Industries TGP-H -060) as a porosity electric conduction sheet, it sank into PTFE dispersion liquid (Daikin Industries make: Pori Flon PTFE dispersion), and this was calcinated at 370 degrees C after desiccation. PTFE was attached and the amount was 20 % of the weight.

[0103] (2) Catalyst support carbon (catalyst ;P. t, VulcanXCmade from carbon;Cabot- 72, amount of platinum support;50wt%) was added using the Nafion solution made from Aldrich of preparation marketing of catalyst bed coating liquid (5 % of the weight) as it is, and the catalyst bed coating liquid which stirs well and consists of a catalyst-polymer constituent was prepared.

[0104] (3) On the porosity electric conduction sheet created with spreading of electrode catalyst bed coating liquid, and the creation above (1) of the electrode by desiccation, the catalyst bed coating liquid prepared above (2) was applied, it dried, and the electrode which consists of an electrode substrate and an electrode catalyst bed was created. Amount 0.5 mg/cm2 with platinum and Nafion were attached, and the obtained electrode was amount 0.3 mg/cm2.

[0105] The thickness of the mixolimnion which the electrode catalyst bed permeated from the cross-section

SEM photograph of this electrode to the electrode substrate was 40 micrometers.
[0106] Using carbon paper (Toray Industries TGP-H -060) as a creation porosity electric conduction sheet of an example 2 (1) electrode substrate, it sank into PFA dispersion liquid (Daikin Industries make: neo chlorofluocarbon PFA AD-2CR), and this was calcinated at 320 degrees C after desiccation. PFA was attached and the amount was 20 % of the weight.
[0107] (2) The carboxymethyl cellulose was added 0.1% of the weight as a thickener in the Nafion solution made from Aldrich of preparation marketing of catalyst bed coating liquid (5 % of the weight). The catalyst bed coating liquid which adds catalyst support carbon (catalyst ;P. t, VulcanXCmade from carbon;Cabot- 72, amount of platinum support;50wt%) to this, stirs to it well, and becomes it from a catalyst-polymer constituent was prepared.
[0108] (3) On the porosity electric conduction sheet created with spreading of electrode catalyst bed coating liquid, and the creation above (1) of the electrode by desiccation, the catalyst bed coating liquid prepared above (2) was applied, it dried, and the electrode which consists of an electrode substrate and an electrode catalyst bed was created. Amount 0.5 mg/cm2 with platinum and Nafion were attached, and the obtained electrode was amount 0.3 mg/cm2.
[0109] The thickness of the mixolimnion which the electrode catalyst bed permeated from the cross-section SEM photograph of this electrode to the electrode substrate was 10 micrometers.
[0110] Like the creation example 2 of an example 3 (1) electrode substrate, using carbon paper (Toray Industries TGP-H -060) as a porosity electric conduction sheet, it sank into PFA dispersion liquid (Daikin Industries make: neo chlorofluocarbon PFA dispersion), and this was calcinated at 320 degrees C after desiccation. PFA was attached and the amount was 20 % of the weight.
[0111] (2) N-methyl pyrrolidone was added condensing the Nafion solution made from Aldrich of preparation marketing of catalyst bed coating liquid (5 % of the weight), and the solvent permutation was performed. The obtained Nafion solution was 10 % of the weight. Catalyst support carbon (catalyst ;P. t, VulcanXCmade from carbon;Cabot- 72, amount of platinum support;50wt%) was added to this, and the catalyst bed coating liquid which stirs well and consists of a catalyst-polymer constituent was prepared.
[0112] (3) On the porosity electric conduction sheet created with spreading of a catalyst-polymer constituent, and the creation above (1) of the electrode catalyst bed by desiccation, the catalyst bed coating liquid prepared above (2) was applied, it dried, and the electrode which consists of an electrode substrate and an electrode catalyst bed was created. Amount 0.5 mg/cm2 with platinum and Nafion were attached, and the obtained electrode was amount 0.3 mg/cm2.
[0113] The static contact angle at the time of putting one drop of catalyst bed coating liquid on this electrode substrate was 90 degrees.
[0114] The thickness of the mixolimnion which the electrode catalyst bed permeated from the cross-section SEM photograph of this electrode to the electrode substrate was 15 micrometers.
[0115] Like the creation example 1 of an example 4 (1) electrode substrate, using carbon paper (Toray Industries TGP-H -060) as a porosity electric conduction sheet, it sank into PTFE dispersion liquid (Daikin Industries make: Pori Flon PTFE dispersion), and this was calcinated at 370 degrees C after desiccation. PTFE was attached and the amount was 20 % of the weight.
[0116] (2) The Nafion solution made from Aldrich of preparation marketing of catalyst bed coating liquid (5 % of the weight) was condensed, and it could be 10 % of the weight. Catalyst support carbon (catalyst ;P. t, VulcanXCmade from carbon;Cabot- 72, amount of platinum support;50wt%) was added to this, and the catalyst bed coating liquid which stirs well and consists of a catalyst-polymer constituent was prepared.
[0117] (3) The electrode which consists of an electrode substrate and a fine porosity structure electrode catalyst bed was created by immersing and drying to butyl acetate immediately after applying the catalyst bed coating liquid prepared above (2) on the porosity electric conduction sheet created with the creation above (1) of spreading of an electrode catalyst bed, wet coagulation, and the fine porosity structure electrode by desiccation. Amount 0.5 mg/cm2 with platinum and Nafion were attached, and the obtained electrode was amount 0.3 mg/cm2.
[0118] The thickness of the mixolimnion which the electrode catalyst bed permeated from the cross-section SEM photograph of this electrode to the electrode substrate was 10 micrometers.
[0119] The staple fiber and expanded graphite powder (the Toyo Tanso make, bulk density 0.14 g/cm3, the mean diameter 100, or 200 micrometers) of a PAN system carbon fiber which were cut into creation die length of 12mm of an example 5(1) porosity electric conduction sheet were mixed to 1:1 by the weight ratio, and it distributed in the sodium carboxymethyl-cellulose water solution. The sheet with which expanded graphite powder adhered to the staple fiber of a carbon fiber was milled on the wire gauze using these

dispersion liquid. The filter paper of two sheets was lightly pressurized on both sides of the sheet in order to remove moisture. Then, the filter paper was removed and the sheet was dried. The roll press of the sheet was carried out after desiccation, and the porosity electric conduction sheet was manufactured. The obtained sheets were 80 g/m2.
[0120] (2) After performing 200 degrees C and heat treatment for 30 minutes for the porosity electric conduction sheet created with the creation above (1) of an electrode substrate in air, it sank in, PFA dispersion (neo chlorofluocarbon PFA dispersion, Daikin Industries, LTD. make) was inserted into the filter paper of two sheets, and it pressurized and dried lightly. Furthermore 400 degrees C and heat treatment of 3 hours were performed, pressurizing this sheet by 14.7kPa (0.15 kgf/cm2), and the porosity electric conduction sheet was manufactured. PFA was attached and the amount was 15 % of the weight.
[0121] (3) N-methyl pyrrolidone was added condensing the Nafion solution made from Aldrich of creation marketing of an electrode catalyst bed (5 % of the weight), and the solvent permutation was performed. The obtained Nafion solution was 10 % of the weight. Catalyst support carbon (catalyst ;P. t, VulcanXCmade from carbon;Cabot- 72, amount of platinum support;50wt%) was added to this, and the catalyst bed coating liquid which stirs well and consists of a catalyst-polymer constituent was prepared.
[0122] (4) On the porosity electric conduction sheet created with spreading of electrode catalyst bed coating liquid, and the creation above (2) of the electrode by desiccation, the catalyst bed coating liquid prepared above (3) was applied, it dried, and the electrode which consists of an electrode substrate and an electrode catalyst bed was created. Amount 0.5 mg/cm2 with platinum and Nafion were attached, and the obtained electrode was amount 0.3 mg/cm2.
[0123] The static contact angle at the time of putting one drop of catalyst bed coating liquid on this electrode substrate was 90 degrees.
[0124] The thickness of the mixolimnion which the electrode catalyst bed permeated from the cross-section SEM photograph of this electrode to the electrode substrate was 15 micrometers.
[0125] The electrode was created like the creation example 2 of an example 6 (1) electrode.
[0126] (2) Film-electrode complex (MEA)
The electrode created in the above (1) was prepared two sheets, and it ****(ed) by making an electrode catalyst bed side counter from the both sides of the proton exchange film (Nafion 112 made from DuPont). The hotpress was performed for this by 150 degrees C and 150MPa, and MEA was created.
[0127] When SEM observation of this cross section of MEA was carried out, the thickness of the mixolimnion which the electrode catalyst bed permeated to the electrode substrate was 10 micrometers.
[0128] (3) MEA created in the fuel cell performance-evaluation above (2) of MEA performed the fuel cell performance evaluation by current-electrical-potential-difference (I-V) measurement. Evaluation cel temperature set hydrogen and cathode (oxidation) gas to air, gas pressure set 70 degrees C and anode (fuel) gas to ordinary pressure, it is horsepower output 450 mW/cm2, and the good engine performance was shown.
[0129] MEA was created like the example 6 using the electrode created in the example 1 of example of comparison 2 comparison.
[0130] In SEM observation of this MEA cross section, the thickness of the mixolimnion to which the electrode catalyst bed permeated the electrode substrate was 30micro.
[0131] Furthermore, although I-V measurement of this MEA was carried out on the same conditions as an example 6, compared with horsepower output 250 mW/cm2 and an example 6, it was low-power output, and was the inferior engine performance.
[0132] The proton exchange resin solution (Nafion solution made from Aldrich) of creation marketing of example 7(1) electrode catalyst bed coating liquid was freeze-dried, frost shattering was performed, and proton exchange resin powder was created. 1.5g of this powder, and catalyst support carbon (catalyst ;P. t, VulcanXCmade from carbon;Cabot- 72, amount of platinum support;50wt%) 3g -- 10g of butyl acetate -- in addition, mixing and distribution were fully performed and catalyst bed coating liquid was created.
[0133] (2) The electrode catalyst bed coating liquid created in the creation above (1) of MEA was used, and it applied and dried to both sides of the commercial proton exchange film (Nafion 112 made from DuPont). From these both sides, the carbon cross (ELAT made from E-TEK) was made to **** as an electrode substrate, and MEA was created.
[0134] When cross-section SEM observation of obtained MEA was performed, the thickness of the mixolimnion which the electrode catalyst bed permeated to the electrode substrate was 5 micrometers.
[0135] (3) MEA created in the fuel cell performance-evaluation above (2) of MEA performed the fuel cell performance evaluation by current-electrical-potential-difference (I-V) measurement. Evaluation cel

temperature set hydrogen and cathode (oxidation) gas into oxygen, gas pressure set 70 degrees C and anode (fuel) gas to ordinary pressure, it is 2 the horsepower output of 800mW/cm, and the good engine performance was shown.
[0136] The solvent 1g, in addition after fully performing mixing and distribution was desiccation-removed for catalyst support carbon (catalyst ;P. t, VulcanXCmade from carbon;Cabot- 72, amount of platinum support;50wt%) in 10g (5% of Nafion solutions made from Aldrich) of proton exchange resin solutions of creation marketing of example 8(1) electrode catalyst bed coating liquid, it ground in them, and powder was obtained. Dioxane 8g was added to this powder, mixing and distribution were fully performed, and catalyst bed coating liquid was created.
[0137] (2) MEA was created using the electrode substrate created in the electrode catalyst bed coating liquid created in the above (1), and the example 5 (1) as well as the creation example 7 of MEA (2). From cross-section SEM observation of obtained MEA, the thickness of a mixolimnion was 5 micrometers.
[0138] (3) MEA created in the fuel cell performance-evaluation above (2) of MEA performed the fuel cell performance evaluation by current-electrical-potential-difference (I-V) measurement. Evaluation cel temperature set hydrogen and cathode (oxidation) gas to air, gas pressure set 80 degrees C and anode (fuel) gas to 0.2MPa(s), it is horsepower output 850 mW/cm2, and the good engine performance was shown.
[0139] The electrode substrate was created like the creation example 5 (1) of an example 9 (1) electrode substrate, and (2).
[0140] (2) Catalyst support carbon (catalyst ;P. t, VulcanXCmade from carbon;Cabot- 72, amount of platinum support;50wt%) was added to the Nafion solution made from Aldrich of creation marketing of an electrode catalyst bed (5 % of the weight), and the catalyst bed coating liquid which stirs well and consists of a catalyst-polymer constituent was prepared. This catalyst bed coating liquid was applied on the Teflon sheet with a thickness of 100 micrometers, it dried, and the electrode catalyst bed was created. Amount 0.5 mg/cm2 with platinum and Nafion were attached, and the obtained electrode catalyst bed was amount 0.3 mg/cm2.
[0141] (3) Two electrode catalyst beds created in the imprint above (2) of the electrode catalyst bed to the proton exchange film were prepared, and it ****(ed) by making an electrode catalyst bed side counter from the both sides of the proton exchange film (Nafion 112 made from DuPont). The roll press of this was carried out, the electrode catalyst bed was imprinted to the proton exchange film, and the proton exchange film with an electrode catalyst bed was created.
[0142] (4) Two electrode substrates created above (1) were made to **** from both sides using the proton exchange film with an electrode catalyst bed created with the creation above (3) of MEA, and MEA was created. From this cross-section SEM observation of MEA, the thickness of a mixolimnion was 5 micrometers.
[0143] (5) MEA created in the performance-evaluation above (4) of MEA performed the fuel cell performance evaluation by current-electrical-potential-difference (I-V) measurement. Evaluation cel temperature set hydrogen and cathode (oxidation) gas to air, gas pressure set 60 degrees C and anode (fuel) gas to ordinary pressure, it is horsepower output 350 mW/cm2, and the good engine performance was shown.
[0144] The proton exchange resin solution (Nafion solution made from Aldrich) of creation marketing of example 10(1) electrode catalyst bed coating liquid was freeze-dried, frost shattering was performed, and proton exchange resin powder was created. 1.5g of this powder, and catalyst support carbon (catalyst ;P. t, VulcanXCmade from carbon;Cabot- 72, amount of platinum support;50wt%) 3g -- 10g of butyl acetate -- in addition, mixing and distribution were fully performed and catalyst bed coating liquid was created.
[0145] (2) The staple fiber and expanded graphite powder (the Toyo Tanso make, bulk density 0.14 g/cm3, the mean diameter 100, or 200 micrometers) of a PAN system carbon fiber which were cut into creation die length of 12mm of electrode substrate coating liquid were mixed to 1:1 by the weight ratio, it fully mixed and distributed at PFA dispersion (neo chlorofluocarbon PFA dispersion, Daikin Industries, LTD. make), and electrode substrate coating liquid was created. PFA was attached and the amount was 15 % of the weight.
[0146] (3) The electrode catalyst bed coating liquid created in the creation above (1) of MEA was used, and it applied and dried to both sides of the commercial proton exchange film (Nafion 112 made from DuPont). From these both sides, the electrode catalyst bed coating liquid created with the above (2) was applied, it dried, and MEA was created.
[0147] From the cross section SEM of obtained MEA, the thickness of a mixolimnion was 5 micrometers.
[0148] (4) MEA created in the performance-evaluation above (3) of MEA performed the fuel cell

performance evaluation by current-electrical-potential-difference (I-V) measurement. Evaluation cel temperature set hydrogen and cathode (oxidation) gas into oxygen, gas pressure set 70 degrees C and anode (fuel) gas to ordinary pressure, it is 2 the horsepower output of 500mW/cm, and the good engine performance was shown.
[0149]
[Effect of the Invention] An electrode with few catalyst **** lumps is obtained by this invention, therefore the use effectiveness of a catalyst improves and the low cost-ized electrode by the amount reduction of catalysts is obtained.
[0150] The electrode of this invention is applied to film-electrode complex (MEA), and also is applied also to usual electrochemistry equipment, especially a polymer electrolyte fuel cell, and is applied also to the mobile and automobile using this fuel cell.

[Translation done.]

CLAIMS

[Claim(s)]
[Claim 1] The electrode characterized by the thickness of this mixolimnion being 20 micrometers or less while this electrode catalyst bed permeates and forming the mixolimnion into this electrode substrate at least in the electrode which consists of an electrode substrate and an electrode catalyst bed.
[Claim 2] The electrode according to claim 1 whose thickness of a mixolimnion is 10 micrometers or less.
[Claim 3] The electrode according to claim 1 or 2 whose electrode substrate is a porosity electric conduction sheet.
[Claim 4] The electrode according to claim 3 whose porosity electric conduction sheet is the thing of the textile-fabrics structure using inorganic conductivity fiber, or non-woven fabric structure.
[Claim 5] The electrode according to claim 4 whose inorganic conductivity fiber is a carbon fiber.
[Claim 6] The electrode according to claim 1 to 5 with which an electrode substrate contains a conductive particle.
[Claim 7] The electrode according to claim 6 whose conductive particle is carbon material.
[Claim 8] The electrode containing the polymer in which an electrode substrate contains a fluorine atom according to claim 1 to 7.
[Claim 9] The electrode according to claim 1 to 8 with which an electrode catalyst bed contains the element more than a kind chosen from the group which consists of platinum, palladium, gold, a ruthenium, and iridium at least.
[Claim 10] The electrode according to claim 1 to 9 with which an electrode catalyst bed contains carbon black.
[Claim 11] The electrode containing the polymer in which an electrode catalyst bed contains a fluorine atom according to claim 1 to 10.
[Claim 12] The electrode containing the polymer in which an electrode catalyst bed has a proton exchange group according to claim 1 to 11.
[Claim 13] The manufacture approach of the electrode according to claim 1 to 12 characterized by applying electrode catalyst coating liquid on an electrode substrate.
[Claim 14] The manufacture approach of an electrode according to claim 13 that the static contact angle of an electrode substrate and electrode catalyst coating liquid is 50 degrees or more.
[Claim 15] Film-electrode complex which consists of an electrode according to claim 1 to 12 and proton exchange film.
[Claim 16] Film-electrode complex according to claim 15 whose proton exchange film is a fluorine atom content polymer.
[Claim 17] Film-electrode complex according to claim 16 which is the polymer which consists of a fluoro alkyl ether side chain with which a fluorine atom content polymer has a sulfonic group, and a fluoro alkyl principal chain.
[Claim 18] The manufacture approach of the film-electrode complex characterized by arranging the proton exchange film between two electrodes according to claim 1 to 12 so that the electrode catalyst bed side of each of said electrode may meet this proton exchange film, making this proton exchange film pinch with said electrode of two sheets, and joining.
[Claim 19] The manufacture approach of the film-electrode complex characterized by performing the process (process A) which prepares an electrode catalyst bed in front flesh-side both sides of the proton exchange film, and the process (process B) which prepares an electrode substrate in both the lateral surface of this electrode catalyst bed in this order.
[Claim 20] The manufacture approach of the film-electrode complex according to claim 19 which is a thing

including the process at which Process A applies electrode catalyst coating liquid on the proton exchange film.
[Claim 21] The manufacture approach of the film-electrode complex according to claim 19 which is that to which Process A applies electrode catalyst coating liquid on an imprint base material, forms an electrode catalyst bed, and imprints this on the proton exchange film.
[Claim 22] The manufacture approach of the film-electrode complex according to claim 19 to 21 which is what carries out coating of the matter with which Process B constitutes an electrode substrate.
[Claim 23] The manufacture approach of film-electrode complex according to claim 22 that the matter which constitutes an electrode substrate is dispersion liquid containing a carbon staple fiber and a fluorine atom content polymer.
[Claim 24] Electrochemistry equipment using an electrode according to claim 1 to 12.
[Claim 25] Electrochemistry equipment using film-electrode complex according to claim 15 to 17.
[Claim 26] Water electrolysis equipment using an electrode according to claim 1 to 12.
[Claim 27] Water electrolysis equipment using film-electrode complex according to claim 15 to 17.
[Claim 28] The fuel cell using an electrode according to claim 1 to 12.
[Claim 29] The fuel cell using film-electrode complex according to claim 15 to 17.
[Claim 30] The fuel cell according to claim 28 or 29 using a solid-state macromolecule mold electrolyte.
[Claim 31] The mobile which makes a fuel cell according to claim 28 to 30 a power source of supply.
[Claim 32] The automobile which makes a fuel cell according to claim 28 to 30 a power source of supply.

[Translation done.]

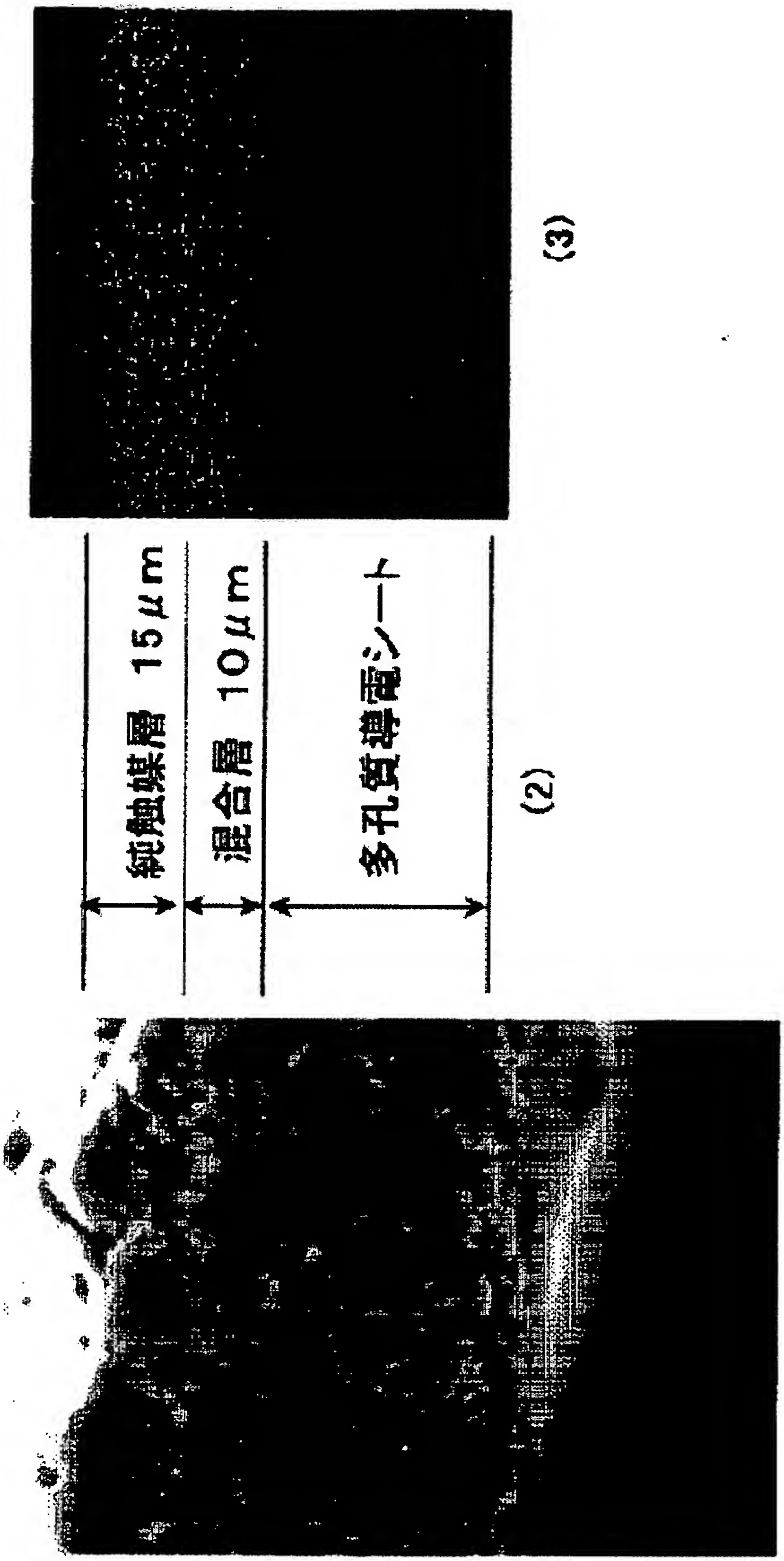
* NOTICES *

JPO and NCIPI are not responsible for any damages caused by the use of this translation.

1.This document has been translated by computer. So the translation may not reflect the original precisely.
2.**** shows the word which can not be translated.
3.In the drawings, any words are not translated.

DRAWINGS

[Drawing 1]



(3) (2) (1)

[Translation done.]